

# Swimming Pool and Spa Water Chemistry



Missouri Department of Health and Senior Services  
Section for Environmental Public Health

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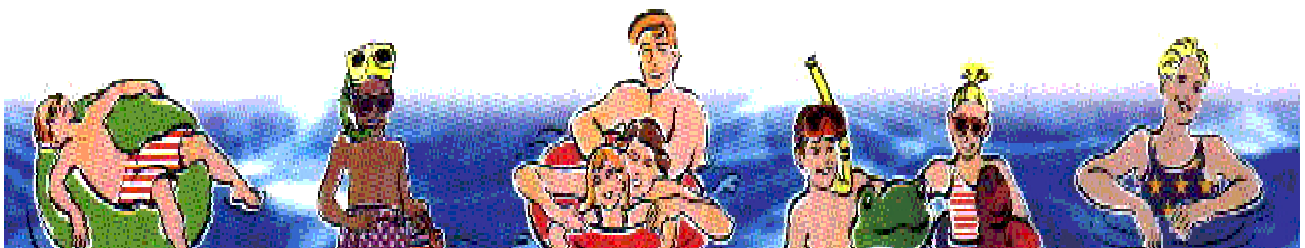
Spa

## **Advanced Pool and Spa Water Chemistry**

Chloramines

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## General

On a hot summer day, who wouldn't want to jump into a cool and refreshing pool? And then, as the sun sets, what better way to relax than to slip into your own backyard spa -- summer or winter?

But enjoying all that requires some regular attention. Remember, the water in your pool and spa is an ever-changing environment that calls for constant and careful monitoring. For some, this means hiring a professional service technician to come by once or twice a week. You can, however, take care of your pool and spa yourself.

The need to treat water has been widely accepted for a long time. Sanitation, especially, is recognized as a means of controlling communicable diseases. The pool operator is expected to provide safe, clean water for bathers.

More recently, however, the importance of mineral saturation, or 'water balance' as it is more popularly known, is recognized by those responsible for maintaining the pool and equipment. Water can become aggressive and destroy pools with corrosion, or it can become scaling and damage the pool with mineral deposits.

The pool operator must learn about the use of chemical agents for sanitation and for control of pH, total alkalinity and calcium hardness. The operator is expected to protect both the swimmers and the pool itself. This chapter is written to present the necessary chemical treatments and sufficient background information to know when and how to use them.

Here's a basic guide to pool and spa water chemistry. It will give you a general outline of the issues that shape routine care.

### Water Sanitizing Components

As you probably know, the occasional addition of new water -- or wholesale water replacement in the case of spas -- isn't enough to keep the water clean and clear of unwanted and often microscopic contaminants.

But worry not! Pool and spa chemists have spent years developing a variety of tests and chemical-treatment methods to keep your pool and spa safe and sparkling clean.

Your goals here are water sanitation and water balance. In other words, you want your levels of sanitizers (such as chlorine or bromine) and your levels of pH, total alkalinity, water hardness and total dissolved solids to all fall within acceptable limits.

And learning to keep these areas in check isn't as complicated as it may seem. To simplify things, we'll explain the relevant topics one at a time.

|                   |   |
|-------------------|---|
| <b>Sanitizers</b> | <p>Sanitizers, or disinfectants, are hardworking chemicals. They also have a killing streak in them -- which is exactly what you want.</p> <p>The important thing to keep in mind is, that for them to do their duty, they have to be present in the pool and spa water at all times. There always needs to be a certain minimum amount -- called a residual -- of sanitizer in your water.</p> <p>What we're saying is, to make sure your pool and spa are protected from bacteria and their friends, you need your sanitizers on 'round-the-clock duty.</p> <p>When you add your sanitizer, therefore, you should be adding enough to kill any existing contaminants in the water -- and create a residual that can neutralize any dirt, debris or germs that may get into the water before you next treat it.</p> <p>That said; let's take a look at some of the most common sanitizing chemicals and equipment available on the market today.</p> |
| <b>Bromine</b>    | <p>Also available on the market today is a chemical sanitizer called bromine. Do note, however, that bromine cannot be stabilized with cyanuric acid. As much as 65 percent of bromine residual can be depleted by the sun in a two-hour time period. Because there is no known way to retain a reliable level of bromine when exposed to sunlight, many experts recommend it for indoor pools or spas only.</p> <p>FYI: The acceptable range of bromine for your pool or spa is from 2.0 to 4.0 ppm.</p> <p>Bromine also has no odor, and dispensing it your spa via a feeder allows it to dissolve at a slow, constant, desirable rate. Just be sure to remove the feeder when your spa is in use.</p> <p>A final note: When using bromine as your sanitizer, you will need to occasionally shock the water with large doses of another chemical to oxidize waste material still in the water. (We'll explain this in more detail below.)</p>       |
| <b>Chlorine</b>   | <p>Chlorine has been somewhat of a wonder drug for pool and spa environments. It has the power to kill bacteria and algae -- and works extremely well in aqueous environments.</p> <p>Chlorine is not invincible, however. Like most chemicals, it has a threshold -- a point at which it has used up all its sanitizing power and can no longer protect your pool and spa water.</p> <p>Chlorine levels are also heavily influenced by evaporation, splash out and destructive UV rays, not to mention a low pH. (You'll read about this last factor in more detail below.)</p>  |

Once added to the water, the "free available" chlorine -- that portion of the chlorine with the killing power -- will sanitize and oxidize the water by attacking undesirables such as bacteria, algae, sweat and oils from your skin, residual soaps, shampoos, perfume and, yes, urine.

As it uses up its killing potential, the chlorine becomes ineffective or it combines with the contaminants and remains in the pool and spa water in the form of chloramines.

FYI: It is the chloramines in your pool and spa water -- not too much "good" chlorine - - that causes a chlorine-like odor and can irritate your eyes and skin.

Indeed, when a pool or spa exudes a chlorine odor and you begin to hear complaints of skin and eye irritation, that is a loud warning that there is not enough chlorine in the water. If this is the case, you should test the water and add the appropriate amounts of sanitizer as soon as possible. (Check out the Testing Your Water section to learn more about this process.)

The recommended level of free available chlorine to keep in your pool is between 1.0 and 3.0 ppm or parts per million. For spas, the recommended level of free available chlorine is between 1.50 and 3.0 ppm.

(For the definition of parts per million and other pool- and spa-related terms, see the Glossary of Terms section).

Another note: We'll address how you measure chlorine and other water-balance levels in another section.

Chlorine is extremely susceptible to sunlight and needs to be regularly monitored. But just as we use sunscreen to protect our skin from the sun, chlorine uses a sunscreen of cyanuric acid. Used this way, cyanuric acid is also commonly called a stabilizer or conditioner.

With its help, chlorine retains its effectiveness. Without going into the chemical whys and wherefores, know that acid works to help keep a fairly consistent chlorine level (a residual) in the water.

Some chlorine-based sanitizers are sold with a dose of cyanuric acid already mixed into the product. One such product is trichlor tablets, (trichloro-s-triazinetri) **are** which are usually placed in a floater, chemical feeder or in the skimmer basket. Another commonly used product is sodium dichlor, (dichloro-striazinetrione) which is a granular substance usually dispersed directly into the pool or spa water, or added via the skimmer.

|                                 |  |
|---------------------------------|--|
| <b>Oxidizers</b>                | <p>OK, you've been reading about oxidizers and oxidizing -- and still have no idea what they are or what they do. Let's find out.</p> <p>Oxidizers work with sanitizers to rid your pool and spa water of pollutants. By definition, sanitizers kill things like algae and bacteria but they work very slowly and inefficiently when trying to remove waste products such as sweat, skin oil, shampoos, soap and urine. This is where you need separate oxidizers.</p> <p>Oxidizers destroy these undesirables. They do their part by breaking down the contaminant's structure, rendering them vulnerable. The sanitizers can then attack and kill the organisms.</p> <p>Some products, such as chlorine, act as both a sanitizer and an oxidizer. Bromine, on the other hand, does not oxidize very well and therefore needs the aid of a separate oxidizing chemical to properly clean your pool and spa water.</p> <p>The marriage of sanitizers and oxidizers is an almost foolproof method of keeping invaders out of your pool and spa water.</p>   |
| <b>Sanitizers - Alternative</b> | <p>Although chlorine and bromine are the most commonly used sanitizers, there are a few alternatives available to also consider. One such alternative is a chlorine generator.</p> <p>Wait, we just discussed chlorine! How is this product different?</p> <p>The liquid or granular chlorine most people are familiar with is added directly to pool or spa water or dispensed through a feeder or similar automated system. Chlorine generators, conversely, actually create chlorine in the pool or spa without you having to measure out any chemicals.</p> <p>These generators are electrical devices that manufacture chlorine from salt added to the water. The resulting chlorine gas is then put directly into the water through the circulation system.</p> <p>Chlorine generators create a residual, which can be tested with a DPD or OTO test kit. (These test kits are described in more detail in a later section.)</p> <p>Another alternative sanitizing source is ozone. No, it's not just the atmospheric layer that protects us from the sun's harmful rays. Rather, the ozone used in pools and spas is a modified version of that gaseous oxygen.</p> <p>To its advantage, ozone works quite well as a sanitizer and an oxidizer. . Because it is a form of oxygen, ozone doesn't last long in an aqueous environment. Once it does its job of ridding the pool and spa water of bacteria and other unwanted matter, the ozone then reverts back to oxygen and either dissolves into the water or escapes into the air.</p> <p>Because it cannot create a residual, an ozonator must be used in conjunction with small amounts of chlorine or bromine -- how much chlorine or bromine depends on how long the ozonator is run each day. One other common kind of sanitizing equipment is an ionizer. This system introduces silver and copper into your pool or spa water through the circulation process. It works well as a sanitizer but does require the addition of an oxidizer.</p> |

## **Chlorination**

This is the most commonly used method of sanitation today. Bromine and iodine are other members of the halogen family of chemicals also used to sanitize water. Other chemicals include ozone, silver and copper compounds. Ultraviolet light is a nonchemical disinfectant. Each of these methods will be covered to some extent, but chlorination is presently the most widely accepted means of treating pool water.

All chlorine - regardless of whether it is introduced as a gas or as a dry or liquid compound when added to water, does exactly the same thing: It forms hypochlorous acid (HOCl) and hypochlorite ions (OCl<sup>-</sup>).

HOCl is the killing form of chlorine; OCl<sup>-</sup> is relatively inactive. However, together, they are free available chlorine (FAC).

Because each of the many chlorinating agents produces the same active form of chlorine, we can ignore the source for now and deal with the process of chlorination in general.

HOCl is an extremely active, powerful chemical. It not only destroys such harmful organisms as bacteria, algae, fungi, viruses, etc., it also destroys impurities that are not removed by filtration. These two processes are called sanitation and oxidation.

## **Sanitation**

Sanitation is the process of destroying organisms that are harmful to People. These organisms, referred to as pathogens, include bacteria, fungi, viruses, etc. Chlorination also controls algae (which are not usually harmful themselves, but may harbor pathogenic organisms). In addition to being unsightly, algae can cause the surfaces around the pool to become slippery and unsafe.

While each of these organisms may require different amounts of HOCl for control, local health officials often establish the required amount for public swimming pools. Very often, local codes will specify an FAC residual of 1.0-3.0 parts per million (ppm), but some might vary from this.

## **Oxidation**

Oxidation is the process of chemically removing organic debris, such as body waste, particulate matter and perspiration, from the water. The process is similar to burning trash in air. It is not important to understand the chemistry involved; it is sufficient to know that enough chlorine in water will chemically "burn" impurities.

The use of chlorine to clean up water is a supplement to filtration, discussed in another chapter. Filters remove the dirt and debris suspended in water, but even the best filter cannot remove dissolved impurities because they are not physically separate from the



water. If the water looks dull or hazy, even though the filter system is operating properly, the operator should consider a shock treatment to oxidize the organic impurities and restore the clarity of the water. Although there are some non-chlorine shock treatments available, the most common method used to shock water is superchlorination.

### **Superchlorination**

Superchlorination is a term that describes an extra large dose (usually 8 to 10 ppm) of chlorine to oxidize organic compounds and kill and remove algae and other contaminants from the water. This is the same as using three to six times the normal dosage of a chlorinating agent. For example, a 50,000-gallon pool requires about four gallons of liquid pool chlorine (12% Available Chlorine) or six pounds of a granular chlorinating compound such as calcium hypochlorite (65% Available Chlorine).

As mentioned, HOCl is the form of chlorine that provides sanitation. Because it is an extremely active chemical, however, it also reacts with organic impurities. When there is enough HOCl present, the impurities are completely oxidized. Combined chlorine is formed when there is an insufficient supply of HOCl or when there is a very high level of organic impurities. Combined chlorine compounds can be oxidized by increasing the HOCl level in the water. The point at which all the organic impurities are oxidized is called the breakpoint. The addition of sufficient chlorine to reach this point is known as breakpoint chlorination.

### **Combined Chlorine**

Combined chlorine is formed by chlorine combining with ammonia and other nitrogen-containing organic compounds. Some sources of these compounds include perspiration, urine, saliva and body oils. These combined forms of chlorine, also called chloramines, are still disinfectants, but they are 40 to 60 times less effective than free available chlorine.

Chloramines kill slowly, so when they are formed in swimming-pool water, the FAC is no longer present for "instant kill" sanitation. Free available chlorine and combined chlorine exist together in many pools. There are simple tests to measure the levels of each. These will be described in detail in another chapter.

In addition to reduced effectiveness against bacteria, chloramines cause eye irritation and the so-called 'chlorine odor' that swimmers complain about. Chloramines have a foul, irritating odor; free chlorine in water in normal concentration has no discernable odor.

### **Breakpoint Chlorination**

When chloramines are known to be present, either by test (over 0.2 ppm combined chlorine) or because of a foul chlorine odor, the continued addition of chlorine causes a corresponding rise in measurable chlorine residual, but eventually, a point is reached at

which addition of chlorine causes a sudden drop in residual. This phenomenon is accompanied by a reduction in eye irritation and chlorine odor.

Investigation reveals that when the total concentration of chlorine in the water reaches seven times the amount of combined chlorine, the oxidation of chloramines and other organic compounds is complete. The point of residual concentration at which this sudden reaction occurs is called the breakpoint. Chlorine remaining or added after the breakpoint is reached exists as free residual chlorine, and all the combined residual is oxidized. The breakpoint varies in its speed and amplitude, depending upon the organic matter present. In some waters, the breakpoint is hardly discernible.

The practice of periodic superchlorination is actually an attempt to pass the breakpoint to rid the water of an accumulation of combined chlorine and potential chlorine-consuming compounds.

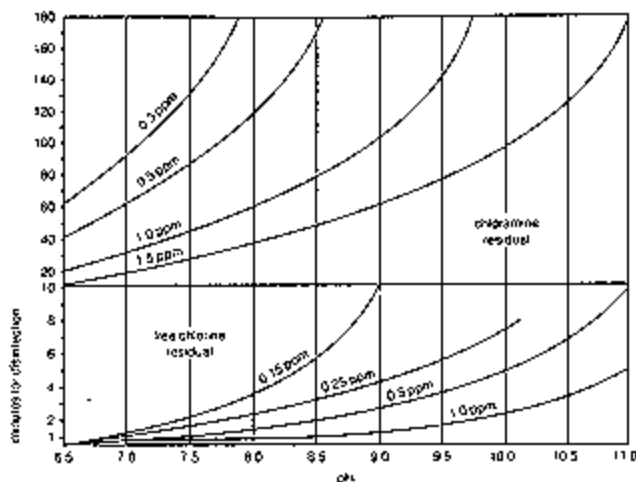


Figure 1 - Graph of breakpoint phenomenon

## Inorganic and Organic Chlorine

Inorganic chlorine compounds such as calcium hypochlorite, sodium hypochlorite and lithium hypochlorite, as well as chlorine gas, are greatly affected by direct sunlight. They require the addition of cyanuric acid to be stabilized when used in outdoor pools. These products are recommended for indoor swimming pools.

Organic chlorine compounds are products combined with cyanuric acid. Sodium dichloro-s-triazinetri-oxide ("dichlor") and trichloro-s-triazinetri-oxide ('trichlor') are both popular stabilized chlorines for water treatment of outdoor pools.

Calcium hypochlorite will support combustion and must never be mixed with carbonated drinks, oils of any type or an organic chlorine product such as "dichlor" or 'trichlor' - explosions can result.

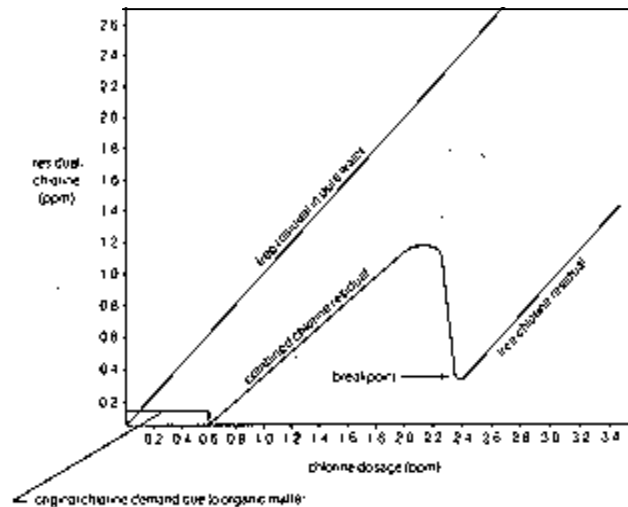


Figure 2 - Disinfection time for free and combined chlorine residuals at various pH values.

## Effect of pH on Chlorine

The pH of water has a definite effect on the efficiency of chlorine as well as on the corrosive properties of water (covered later in this chapter.) For now, we will consider only the effect of pH on sanitation.

It can be seen in Table 2.a that free chlorine is most efficient in pH ranges below the ideal range of 7.2-7.6. Some pool operators do, however, maintain pH levels higher than the ideal range. They should also maintain appropriately higher FAC levels to provide the same concentration of the active HOCL form.

For example, at a pH of 8.0, 21% (about 1/5 of the FAC is in the active form. At that pH level, it would take 2.5 ppm of FAC to provide about 0.5 ppm of HOCl. At a pH of 7.5, about 1/2 (50%) of the FAC is in the active HOCl form. At that pH level, it would take only 1.0 ppm of FAC to provide the same 0.5 ppm of HOCl. For this reason, many authorities recommend that the pH of pools be maintained in the range between 7.2 and 7.6 and as close to 7.5 as practical. These conditions are also considered to be most comfortable for the swimmers' eyes and skin.

| HOCl                      | H <sup>+</sup> | OCl <sup>-</sup>               |
|---------------------------|----------------|--------------------------------|
| Hypochlorous Acid         |                | Hypochlorite Ion               |
| Killing Agent             | Hydrogen Ion   | Inactive, but stable form      |
| Active, but unstable form |                |                                |
| % Chlorine as HOCl        | pH             | % Chlorine as OCl <sup>-</sup> |
| 90                        | 6.5            | 10                             |

|    |     |    |
|----|-----|----|
| 73 | 7.0 | 27 |
| 66 | 7.2 | 34 |
| 45 | 7.6 | 55 |
| 21 | 8.0 | 79 |
| 10 | 8.5 | 90 |

## Chlorine Gas (Cl<sub>2</sub>)

Chlorine gas has 100% available strength, is very toxic and can be lethal if an operator is overcome by it. This form of chlorine is the most economical, pound for pound, but the laws regarding safety practices and the intricate feeding equipment it requires make it a feared method of water sanitation. Chlorine gas for pool use is contained under pressure in steel tanks as large as one ton. The gas is green in color and heavier than air.

Strict adherence to the following practices is required for minimum safety:

1. Chlorine tanks should always be stored indoors in a fire-resistant building.
2. Tanks and chlorinator must be kept in a separate room with a vent fan capable of complete air exchange in one to four minutes.
3. Tanks must be chained or strapped to a rigid support to prevent accidental tipping.
4. A self-contained air supply gas mask must be immediately available in case of emergencies.
5. The chlorinator and all tanks should be checked daily for leaks. A small amount of ammonium hydroxide (household ammonia) on a piece of cloth produces white vapor in the presence of chlorine.

## Sodium Hypochlorite (NaOCl)

Sodium hypochlorite is a clear, slightly yellow liquid solution used in dilute form as common household bleach. In its commercial form, it provides 12% to 15% available chlorine. The chemical is usually introduced to pool water through a chemical feeder, but it can be poured directly into the pool for a quick increase in chlorine residual. It has no sediment or precipitate and raises Total Dissolved Solids (TDS). This chemical has a pH of 13 and causes a significant increase in the pool's pH. The occasional addition of muriatic acid or sodium bisulfate can correct the increased pH, however.

Sodium hypochlorite is not stable in storage and gradually loses strength, especially in sunlight. If stored in a dark, cool room, it has a one-month shelf life.

Dilute solutions of sodium hypochlorite can be used for poolside sanitation and for disinfecting and cleaning decks. The chemical should not be spilled directly on clothes

and should be immediately washed off if it gets on the skin. However, its safety and low cost has made this a very popular chlorinating agent.

### Calcium Hypochlorite (Ca(OCl)<sub>2</sub>)

Calcium hypochlorite is available in granular or tablet form. It provides 65% available chlorine by weight and remains stable if stored in a dry, cool area. The chemical can be dissolved and introduced to the pool as a liquid, or it can be added in dry form. When applied directly to the pool, it may cause a temporary cloudiness. Direct applications should be broadcast evenly over the water surface to avoid bleaching the pool bottom as a result of having a concentrated amount in one spot. This must be done when no bathers are in the pool.

This chemical, when contaminated by or mixed with an organic compound, can produce a fire. A good rule is never to mix calcium hypochlorite with another chemical or store it in anything but the original container. Mix the chemical into water not water into the chemical. Calcium hypochlorite should not be handled with bare hands and must be kept off the operator's clothes.

As a chlorinating agent, calcium hypochlorite will slightly increase pool pH. It has a pH of 11.8. Operators of gas-chlorinated pools often keep a supply on hand for emergency use or for a quick charge when superchlorinating. Dissolved in water, calcium hypochlorite can be used as a sanitizing agent for decks and locker rooms.

|                                | <b>GAS<br/>CHLO-<br/>RINE</b> | <b>SODIUM HYPO<br/>CHLORITE</b> | <b>CALCIUM HYPO<br/>CHLORITE</b> | <b>LITHIUM HYPO<br/>CHLORITE</b> | <b>DICHLOR</b>      | <b>TRICHLOR</b>       |
|--------------------------------|-------------------------------|---------------------------------|----------------------------------|----------------------------------|---------------------|-----------------------|
| <b>%AVAILABLE<br/>CHLORINE</b> | 100%                          | 12.15%                          | 65-75%                           | 35%                              | 56% OR<br>62%       | 90%                   |
| <b>pH EFFECT</b>               | LOWERS<br>(pH <<br>1.0)       | RAISES<br>(pH 13.0)             | RAISES<br>(pH 11.8)              | RAISES<br>(pH 10.7)              | NEUTRAL<br>(pH 6.9) | LOWERS<br>(pH 2.9)    |
| <b>LOST TO<br/>SUNLIGHT</b>    | YES                           | YES                             | YES                              | YES                              | NO                  | NO                    |
| <b>PHYSICAL<br/>APPEARANCE</b> | GAS                           | LIQUID                          | GRANULAR &<br>TABLETS            | POWDER                           | GRANULAR            | GRANULAR &<br>TABLETS |

### Lithium Hypochlorite (LiOCl)

Lithium hypochlorite is a newer entry in the field of chlorinating agents. Its cost is greater than other hypochlorites, and it provides only about 35% available chlorine. However, the chemical is fast dissolving and totally soluble in water, and pH tends to rise more slowly with its use than with other chemicals. It has a pH of 10.7. Lithium hypochlorite should not be mixed with organic compounds, but it is safer to store and use than calcium hypochlorite.

## **Chlorinated Isocyanurates (Stabilized Chlorine)**

This family of chemicals is in wide use for swimming pool chlorination. The family is composed of sodium dichloro-s-triazinetriene and trichloro-s-triazinetriene - chlorine compounds that contain cyanuric acid (stabilizer). The dichlor is more soluble and provides 56% or 62% available chlorine, depending on formulation. dichlor provides 90% available chlorine and is used when a slow release of chlorine over a period of time is desired. The dichlor compound has little effect on pH, while trichlor is extremely acid (pH 2.8-3.0). Dichlor can be added directly to the pool; trichlor is generally fed through an erosion-type feeder, but never through the skimmer basket.

The major effect of cyanuric acid on hypochlorous acid (HOCl) is to keep it from being decomposed by ultraviolet (LTV) light such as contained in sunlight.

Because it is readily decomposed by LTV light, the dosage of a chlorinating agent that is sufficient for an indoor pool is dissipated rapidly in an outdoor pool. Cyanuric acid bonds with the available chlorine in a manner that does not use up the chlorine. At high stabilizer levels (over 100 ppm), chlorine's efficiency may be reduced. The operator should consult the local codes and manufacturers' recommendations on the proper use of stabilizers.

## **Chlorination Summary**

- Chlorination both sanitizes and cleans the water by oxidizing organic impurities.
- A free chlorine residual of 1.0-3.0 ppm is preferred. Combined chlorine should not exceed 0.5 ppm and may be destroyed by breakpoint chlorination.
- Proper pH control (7.2-7.6) provides better chlorine efficiency.
- When cyanuric acid is used in an outdoor pool, chlorine consumption is reduced, because the chlorine degradation caused by LTV light is reduced.
- There are many chlorinating agents available but each provides HOCl, the active chemical specifically for disinfecting.

## **ALTERNATIVE SANITIZERS**

Other members of the halogen family - bromine and iodine - are used for treating pool water. New developments in the use of ozone, ultraviolet light, ionization of salts and other chemical compounds continue to provide new challenges and techniques in water treatment.

### **Bromine**

Although bromine in its elemental form is a liquid, it is not available for swimming pool disinfection in that form. Elemental bromine is a heavy, dark brown, volatile liquid with fumes that are toxic and irritating to eyes and respiratory tract. For pool sanitation, bromine compounds are sold in two solid forms - a two-part system that uses a bromide

salt dissolved in water and activated by addition of a separate oxidizer; and a one-part stick or tablet that contains both bromine and an oxidizer and is dispensed by an erosion-type feeder.

The chemistry of bromine is similar in many respects to the chemistry of chlorine; however, bromine cannot be used for shock treating.

Bromine has a pH of 4.0-4.5. When bromine is added to water and an oxidizer is present, the bromine forms hypobromous acid (HOBr) and hypobromite ions (OBr<sup>-</sup>). Like chlorine, the percentage of each is affected by pH. However, the effect is not as dramatic as it is with chlorine. Table 2.c displays the effect of pH on bromine. Like chlorine, bromine combines with organic impurities to form combined bromine or bromamines. However, combined bromine is still an effective sanitizer, and it does not smell. Because of this, bromine is popular for spas.

| <b>HOBr<br/>Hypobromous Acid<br/>% Bromine as HOBr</b> | <b>pH</b> | <b>OBr-<br/>Hypobromite Ion<br/>% Bromine as OBr-</b> |
|--|-----------|---|
| 100.0  | 6.0       | 0.0   |
| 99.4   | 6.5       | 0.6   |
| 98.0   | 7.0       | 2.0   |
| 94.0   | 7.5       | 6.0   |
| 83.0   | 8.0       | 17.0  |
| 57.0   | 8.5       | 43.0  |

## **Iodine**

Potassium iodide (KI) is a white, crystalline chemical that dissolves in water without a precipitate. When activated by the presence of an oxidizer, it is converted to hypoiodous acid (HOI). Iodine does not react with ammonia to produce iodamines; it does not bleach hair or swimming suits, and eye irritation is practically nonexistent.

Other chemicals (usually chlorine) must be used in conjunction with iodine to control algae and oxidize organic matter. The sole effect of iodine is to produce bacteria-free water..

## **Ozone**

Ozone was first used as a water sanitizer in France in the early 1900s. It is the most popular method of treating drinking and pool water throughout Europe. Ozone is one of the strongest oxidizers available for treating swimming and spa water and is growing in popularity in the U.S.A. It kills bacteria and oxidizes organic compounds including chloramines, soaps, oils and bather wastes and does not alter the water's pH. Due to

limitations of the amount of ozone that can be economically introduced to pool and spa water, algae growth is not eliminated and may possibly increase.

Two systems have been developed for the production of ozone for pool and spa water. The most common European method - and the most expensive - is the Corona Discharge. This method generates ozone by exposing pressurized, dried air to high-voltage electricity. The ozone gas is then directed into the bottom of the pool and seen as very small bubbles rising to the surface. The ozone can be introduced into a separate chamber or directly to the pool.

The Ultraviolet (LTV) or photochemical method of ozone production passes the pressurized, dried air next to a UV bulb within a chamber, where the UV rays bombard the oxygen molecules and produce ozone. A single LTV lamp is capable of treating approximately 10,000 gallons of water. The UV method is more common for spas or private small pools and is less expensive to operate. The LTV method cannot match the output of the Corona Discharge method.

Once it has done its job as an oxidizer, ozone reverts to oxygen and improves both smell and taste of the water. This factor is worth noting, especially for indoor pools. Ozone has to be continually generated, because its effectiveness is about 22 minutes while the gas remains in the water. Ozone offers no continuous residual, and because it is not effective against algae growth, most manufacturers recommend that ozone be introduced with a halogen such as chlorine or bromine.

Testing of ozone residual is in parts per billion (ppb). Test kits are available that use DPD as the reagent and color calibrations that indicate readings from 0 to 100 ppb. Testing with the use of an Oxidation Reduction Potential (ORP) meter is effective, and a minimum level of 650 millivolts is recommended. Because ozone of the smallest residual is effective and adequate for treating water, when combined with chlorine or bromine, a test reading of either is an indication of the effectiveness of the ozone.

## **ELECTROLYTIC CELLS**

Electrical devices (chlorine generators) have been developed that produce chlorine from salt dissolved in the pool water or within a separate salt-solution (brine) chamber. This method is becoming popular in Australia and some European countries. Because of their use on spacecraft, development of metals that are used for electrodes has been rapid. There is a real future for this concept in sanitizing water.

### **Brine Method**

The brine type of chlorine generator passes 4 to 16 D.C. voltage of about 20 amps through two chambers. One chamber houses the positive (anode) electrode within a brine solution of salt and distilled water, while the second chamber houses the negative (cathode) electrode, also in water. Chlorine is formed as a gas at the anode and sodium hydroxide (caustic soda) at the cathode. Chlorine gas is drawn off through a tube and



introduced into the pool or spa water. Some systems use the caustic soda as a neutralizer for pH balance. This design is similar to those used for producing chlorine gas commercially and can be designed for any size pool.

### **In-Line Method**

The in-line type of chlorine generator is located within the pool or spa circulation system, past the filters. A low concentration of salt is added directly to the pool. The electrolytic cell has been designed for smaller pools or spas and requires a current of 5 to 15 amps with 5 to 35 volts D.C. The production of chlorine gas, caustic soda and hydrogen gas passes directly into the pool or spa water.

The water passing the electrodes is superchlorinated and thereby reduces the build-up of chloramines. The caustic soda aids in balancing pH. The control unit is capable of reversing the charge on the electrodes to eliminate scale build-up. The chlorine generated from salt will, after use, revert back to salt, and the process starts all over again. The addition of salt is reduced greatly by this recycling.

### **Automation**

Chlorine generators activated by ORP sensors have produced a system that reacts to fluctuations in swimmer load and oxidizing demands for algae prevention. In-line units in large pools have been coupled with electronic control systems to offer a means of continuously treating the water.

## **SILVER**

The bactericidal properties of silver nitrate and Argyrol are well known in medical practice. Silver ions are introduced to water by electrolysis or by passing a current through a silver electrode. The primary limiting factors in its use in swimming pools are the high cost of silver and the fact that its bactericidal action is quite slow. Silver is also photosensitive and may cause a black deposit to form on the walls.

## **NON-CHLORINE OXIDIZERS**

Products are available to oxidize body wastes and organic materials and to reduce combined chlorine or chloramines. These products are not sanitizers and are used as an alternative to superchlorination for oxidizing only. Non-chlorine oxidizers are useful for clearing cloudy water in heavily used pools located in areas where health codes place upper limits on free available chlorine readings.

## **OTHER POOL CHEMICALS**

The greatest use of chemical products is in the bactericidal treatment of pool water. Many special conditions, however, create requirements for additional chemical treatment.

## **Flocculants**

Aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), commonly called alum, is used as a filter aid and as a coagulant and settling agent for water turbidity. Alum 'floc' is a white, gelatinous substance that attaches to free-floating matter in water to form larger, heavier-than-water particles, which settle to the bottom of the pool. Alum floc is especially effective on sand filter beds. The floc partially fills the voids in the sand bed and holds organic debris in its suspended gelatinous coating.

Alum is introduced as a filter aid at the most convenient entry point ahead of the filter. The chemical feed, hair and lint strainer or skimmer are effective points of introduction. However, to coagulate particles in pool water, a powdered alum is broadcast over the pool surface at the rate of two ounces per square foot of surface area and is permitted to stand overnight or for a minimum of two hours. After standing, the pool should be vacuumed with minimal agitation to prevent the floc from breaking apart. It is recommended when using alum as a water clarifier or a filter floc that the pool water be adjusted to pH of 7.6-7.8.

Flocculants aids, with a combination of ingredients, sold under various trade names, have been used to produce a heavier or more stable floc. Colloidal silica, a clay called bentonite and a new family of organic polyelectrolytes are available.

## **Algaecides**

The chemistry of algaecides is complex, because 46 species of clean-water algae exist. Some algaecides work better on one kind of algae than on another.

Planktonic clean-water algae float on the surface. Other types attach themselves to rough spots on the pool walls and floor and are very difficult to remove. Clean-water algae may be blue-green, red, brown or black and can cause tastes, odors, turbidity and slippery spots, as well as increased chlorine demand.

Sunlight, temperature, pH, bacteria, chlorine residual and the mineral content of the water affect the presence and growth rate of algae. Algae can be introduced to a pool by wind-borne debris, rain and falling leaves, or they may be present in the source from which the pool is filled.

Preventing algae growth by chlorination is usually not a problem, but removing existing algae from a pool can be difficult. If algae get a firm start on the side or bottom of a pool, draining the pool is sometimes more practical if the local water table is not too high to allow it. The pool should be thoroughly washed down with a chlorine solution.

Sunlight is necessary to the growth of algae, so it is a much greater problem in outdoor pools. If not controlled, algae can spread rapidly, turning an entire pool dark green in as little as a day or two.

Pools that consistently maintain a high free chlorine residual concentration are seldom troubled by algae. Maintaining free available chlorine and superchlorinating are the best preventative measures. Combined chlorine is not as effective as free chlorine in preventing algae growth, and bromine and iodine are even less effective.

An algae inhibitor is a commercial product that acts as a penetrating or wetting agent to allow the chlorine to be more effective. Algae inhibitor is said to control all types of algae growth and provide a stable backup system to chlorine. It is not pH sensitive, does not evaporate, concentrates on surfaces of the algae and is a powerful wetting agent.

### **Chelating or Sequestering Agents**

Many stains around main drains and inlets have to be cleaned by hand, but the stains can be kept from returning. Sequestering agents increase the ability of water to hold metals in solution instead of precipitating out to form stains. Chelating agents remove iron and other metals from the water and the pool walls. Pools with high iron content use a chelating agent as part of routine water treatment.

### **Degreasers**

There are commercial acids and biodegradable detergents that effectively clean D.E. filter bags and filter sand. Each product has its own ability to degrease and rejuvenate filters. Each filter system has its own individual solution for doing the job.

### **Defoamers**

Foam or suds is a chronic problem for most spas. Occasionally, a box of detergent is thrown into the water as a prank, and a defoamer made specifically for pools and spas is necessary to remove the foam. A bottle of defoamer is handy to have on hand as a safeguard.

### **Cyanuric Acid**

Chlorine in outdoor pools must be shielded from the degrading effects of the sun's ultraviolet (UV) rays. Cyanuric acid is used in outdoor pools with the inorganic chlorines such as calcium hypochlorite, sodium hypochlorite, lithium hypochlorite and chlorine gas.

It is recommended that the cyanuric-acid level be 30-50 ppm with a maximum of 100 ppm and a lower limit of 10 ppm. The level of cyanuric acid is reduced by dilution due to filter backwashing, bather dragout or dumping. To meet health codes, pools above 100 ppm need to be drained of about 20% of volume, and fresh water added. Four pounds of cyanuric acid will offer a reading of 50 ppm in 10,000 gallons of water. Cyanuric acid has a pH of 4.0, and if added to a gas-chlorinated pool, the addition of one-third of a pound of soda ash per pound of cyanuric acid is recommended.

'Chlorine Lock,' a term given to a condition once thought to be produced from high cyanuric-acid levels tying up free available chlorine, has been proven false by the industry. Generally, high cyanuric acid levels of 400 ppm or higher are associated with excessive Total Dissolve Solids (TDS) or combined chlorine or chloramines and not "Chlorine Lock".

## Balanced Water

There's more to taking care of a pool and spa than just keeping the water clean. You also have to make sure the water is properly balanced.

Water that is not balanced -- that is too acidic or too basic -- can cause bather discomfort, cloudy water and damage to the pool and spa surfaces and equipment.

Water follows certain natural laws, just like other things around us. Unsupported objects fall to the ground, and this is called the law of gravity. It is the nature of water to dissolve the things it contacts until it becomes saturated. It is possible for it to dissolve too much and become over saturated, at which point the water loses its excess material by precipitation. This is governed by the laws of *chemical equilibrium*, more commonly referred to as *water balance* (see Table 3.a).

Many operators are already familiar with this subject to some degree. A commonly used tool in determining the degree of saturation in pool water is the Langeleir Index. Originally devised for the complicated and variable conditions found in industrial water treatment (boilers, cooling towers, heat exchangers etc.), it has been simplified for use with the swimming pool water. The degree of saturation is determined by the pH, temperature, total alkalinity and calcium hardness found in the pool water.

The pH reading is used directly. The temperature factor (TF), alkalinity factor (AF) and calcium factor (CF) are read from the Table, using the test values obtained from a pool test kit.

The constant (12.1) includes a factor for Total Dissolved Solids (TD), assuming a value of less than 1000 ppm TDS. When the TDS is found to be higher (1000-2000 ppm) a value of 12.2 should be used for the constant.

$$\text{Saturation Index} = \text{pH} + \text{TF} + \text{CF} + \text{AF} - 12.1$$

To determine whether the pool water is aggressive (under saturated) or scale forming (over saturated), the operator would

1. Complete the water testing
2. Run the Water Balance Test from Online Water Testing

### Langelier Index - Saturation Table

| Temp F | TF  | Calcium Hardness Expressed As PPM CaCO <sub>3</sub> | CF  | Total Alkalinity Expressed As PPM CaCO <sub>3</sub> | AF  |
|--------|-----|---|-----|---|-----|
| 32     | 0.0 | 5   | 0.3 | 5   | 0.7 |
| 37     | 0.1 | 25  | 1.0 | 25  | 1.4 |
| 46     | 0.2 | 50  | 1.3 | 50  | 1.7 |
| 53     | 0.3 | 75  | 1.5 | 75  | 1.9 |
| 60     | 0.4 | 100   | 1.6 | 100   | 2.0 |
| 66     | 0.5 | 150   | 1.8 | 150   | 2.2 |
| 76     | 0.6 | 200   | 1.9 | 200   | 2.3 |
| 84     | 0.7 | 300   | 2.1 | 300   | 2.5 |
| 94     | 0.8 | 400   | 2.2 | 400   | 2.6 |
| 105    | 0.9 | 800   | 2.5 | 800   | 2.9 |
| 128    | 1.0 | 1000  | 2.6 | 1000  | 3.0 |

**TF - Temperature Factor - CF - Calcium Factor - AF - Alkalinity Factor**

### CHEMICAL BALANCING

The term balancing has many meanings when referring to pool and spa water chemistry and conditions. The following summarizes these various definitions and conditions.

#### **Corrosive vs. Non-corrosive**

Two chemical levels exist that determine corrosive conditions. Both conditions are serious and costly if not checked. (1) If pH is lower than 7.0, the water is considered acidic and it will attack and dissolve metals, especially the copper pipes in the heat exchanger located in the pool heater. (2) When the saturation index is a negative value, the water will attack or dissolve the calcium found in the pool-shell plaster or grouting between pool tiles.

## **Irritating vs. Non-irritating**

Both the human skin and eyes will react to chemical extremes. There are two conditions that will cause inflammation and irritation to the eyes. The human eye has a pH of 7.3-7.5 and will become extremely uncomfortable when pH is below 7.0 and above 8.0. The second condition is when the combined-chlorine level is above .5 ppm and the chloramines cause the irritation. Both conditions should never occur if hourly testing is accomplished and recommended chemical levels are maintained.

## **Staining vs. Non-staining**

Two conditions exist that cause iron or copper metal staining of a pool shell, especially a plaster surface. Excessive iron content in the water supply may cause a reddish or rust discoloration at the inlets of the pool if a chelating agent is not used to hold the metal in suspension.

Copper staining creates a blue or blue-green discoloration of a plastered pool shell. This condition is created when the pH is lower than 7.0 for long periods, and the acidic water attacks the copper tubing found in the heater's heat exchanger. This can become very costly if walls require sanding or sandblasting and if it is necessary to replace a heat exchanger.

## **Clarity**

Water clarity is a result of proper chemical balance, adequate circulation and filtration. Most often, cloudy water conditions are caused by low chlorine, high alkalinity, high pH, high TDS or a combination of these. It is possible to have proper chemical readings and still have cloudy water during high swimmer load if the flow rate of the circulation system is low or if there is poor filtration.

## **Water Saturation Summary**

- Properly balanced or saturated water prevents damage to the pool and equipment. Unsaturated water corrodes plaster walls, fixtures, plumbing, etc., and causes staining. Oversaturated water deposits scale or becomes cloudy. The operator needs to test and control pH, total alkalinity, and hardness in order to maintain balanced water.
- Proper pH control (7.2 to 7.6) ensures: (1) the proper form of carbonate alkalinity for saturation, and (2) the proper form of HOCl for sanitizer efficacy.
- Soda ash is used to raise pH. Acids are used to reduce both pH and total alkalinity, depending on how they are applied.
- Sodium bicarbonate is used to raise total alkalinity.
- Alkalinity of 80-120 ppm is preferred for both pH buffering and calcium carbonate saturation.
- Calcium hardness of 200 ppm, or more, is preferred for proper calcium carbonate saturation and for avoiding soft-water scale found in spas and hot tubs.

- Calcium chloride is used to raise calcium hardness. The best means of lowering hardness is to drain off some of the water and refill with fresh water.

To help you get a handle on what water balance means -- and how you can maintain it - let's look, one at the time, at the factors that shape your water quality.

## Chlorine

Is acting as the main sanitizer to kill algae and bacteria in the pool water. The level should be between 2.0 and 3.0 on your test kit. During hot weather, high readings are better.

### Free Available Chlorine (FAC)

All chlorine - regardless of whether it is introduced as a gas or as a dry or liquid compound when added to water, does exactly the same thing: It forms hypochlorous acid (HOCl) and hypochlorite ions (OCl<sup>-</sup>).

HOCl is the killing form of chlorine; OCl<sup>-</sup> is relatively inactive. However, together, they are **Free Available Chlorine (FAC)**.

### Combined Chlorine

Combined chlorine is formed by chlorine combining with ammonia and other nitrogen-containing organic compounds. Some sources of these compounds include perspiration, urine, saliva and body oils. These combined forms of chlorine, also called chloramines, are still disinfectants, but they are 40 to 60 times less effective than free available chlorine.

Chloramines kill slowly, so when they are formed in swimming-pool water, the FAC is no longer present for "instant kill" sanitation. Free available chlorine and combined chlorine exist together in many pools. There are simple tests to measure the levels of each. These will be described in detail in another chapter.

In addition to reduced effectiveness against bacteria, chloramines cause eye irritation and the so-called 'chlorine odor' that swimmers complain about. Chloramines have a foul, irritating odor; free chlorine in water in normal concentration has no discernable odor.

### Total Chlorine

Simply stated, there are three types of chlorine test readings: free available chlorine (FAC), combined chlorine and total chlorine. Free plus combined equal total. Only the free chlorine is effective in killing bacteria or algae. A high level of combined chlorine indicates the need for shocking or super chlorinating to eliminate it.

## Bromine

Although bromine in its elemental form is a liquid, it is not available for swimming pool disinfection in that form. Elemental bromine is a heavy, dark brown, volatile liquid with fumes that are toxic and irritating to eyes and respiratory tract. For pool sanitation, bromine compounds are sold in two solid forms - a two-part system that uses a bromide salt dissolved in water and activated by addition of a separate oxidizer; and a one-part stick or tablet that contains both bromine and an oxidizer and is dispensed by an erosion-type feeder.

The chemistry of bromine is similar in many respects to the chemistry of chlorine; however, bromine cannot be used for shock treating.

Bromine has a pH of 4.0-4.5. When bromine is added to water and an oxidizer is present, the bromine forms hypobromous acid (HOBr) and hypobromite ions (OBr<sup>-</sup>). Like chlorine, the percentage of each is affected by pH. However, the effect is not as dramatic as it is with chlorine. Table 3.2.a displays the effect of pH on bromine. Like chlorine, bromine combines with organic impurities to form combined bromine or bromamines. However, combined bromine is still an effective sanitizer, and it does not smell. Because of this, bromine is popular for spas.

| <b>HOBr</b>              |           | <b>OBr<sup>-</sup></b>              |
|--------------------------|-----------|-------------------------------------|
| <b>Hypobromous Acid</b>  |           | <b>Hypobromite Ion</b>              |
| <b>% Bromine as HOBr</b> | <b>pH</b> | <b>% Bromine as OBr<sup>-</sup></b> |
| 100.0                    | 6.0       | 0.0                                 |
| 99.4                     | 6.5       | 0.6                                 |
| 98.0                     | 7.0       | 2.0                                 |
| 94.0                     | 7.5       | 6.0                                 |
| 83.0                     | 8.0       | 17.0                                |
| 57.0                     | 8.5       | 43.0                                |

## pH

Is the level of how acidity the pool water. You must maintain a good pH level or your chlorine will not work effectively. The level should be between 7.2 and 7.6.

The most fragile and arguably the most important component of water balance is pH, a reading that indicates how acidic or basic your pool and spa water is.



Without going into the entire story of what pH is and how it works, suffice it to say here that it's important to monitor it because it has an impact on your sanitizer effectiveness, not to mention your pool or spa's surfaces, equipment -- and you.

Here are the most common problems associated with both high or low pH levels:

| High pH Readings          | Low pH Readings                 |
|---------------------------|---------------------------------|
| Poor sanitizer efficiency | Poor sanitizer efficiency       |
| Cloudy water              | Etched or stained plaster       |
| Shorter filter runs       | Corroded metals/equipment       |
| Scale formation           | Skin and eye irritation         |
| Skin and eye irritation   | Destruction of total alkalinity |

The ideal pH range for pools is between 7.4 to 7.6. For spas, the range is 7.2 to 7.8. Any reading below 7.4 for pools or 7.2 for spas means your water is acidic.

To correct the situation, you would add soda ash or sodium bicarbonate, two substances available at your local pool/spa supply store. Note: You should not add soda ash to a spa as you would to a pool -- it is too strong for the small spa environment.

If the pH reading is above 7.6 for pools or 7.8 for spas, it means the water is basic or alkaline. To bring the pH level down in pools, you'll need to add some liquid muriatic acid to the water. Muriatic acid is also available in pool/spa supply stores.

Here again, you need to take special care with your spa: Liquid muriatic acid is too powerful for the small volumes of water found in spas. Therefore, experts do not recommend using muriatic acid in spas. Instead, you should add dry acid.

pH is a number between 0 and 14 that indicates how acidic or basic a solution is (See Figure 5.4). Pure distilled water has a pH of 7.0 and is neither acidic nor basic. Water with a pH of lower than 7.0 is said to be acidic, and the smaller the number, the more acidic the water is. On the other hand, water with a pH greater than 7.0 is basic, and the larger the number, the more basic the water.

Acidic compounds, such as sodium bisulfate or muriatic (hydrochloric) acid, lower the pH of water. Alkaline compounds, such as soda ash or sodium hydroxide, raise the pH of water. Alkaline compounds are, therefore, basic. The use of both alkaline and basic to refer to high pH, and to compounds that raise the pH, causes some confusion with the *alkalinity* of water. The difference between total alkalinity and pH is discussed later.

In addition to the effects of pH on the chlorination process, there is also an effect on the total alkalinity of water. This plays a major role in the degree of calcium carbonate saturation. This dual effect makes the control of pH very important to the pool operator.

Molecules of water (and other substances) break up into electrically charged particles called ions. Water separates into positively charged hydrogen atoms, called hydrogen

ions, and negatively charged particles containing one hydrogen atom and one oxygen atom.

The pH of a solution does not indicate the total amount of an acid or base in the solution, but only how much of it is ionized. This point is very important in the subject of total alkalinity, which is explained further on in this chapter.

pH is a very complicated subject, and the above explanation has been deliberately simplified to give sufficient, accurate information for swimming pool operation. Chemists would not accept it as complete, but it will do for this discussion.

Accurate control of the pH of swimming pool water is essential. The effects of pH upon flocculants, bactericides, algae growth, equipment, maintenance and bather comfort will be discussed throughout the Handbook.

The pH of swimming pool water must be kept slightly above 7.0 and must never exceed 7.8. Most state health departments recommend that the pH of swimming pool water be kept between 7.2 and 7.6. This range provides the best conditions for precipitation of flocculants on conventional sand filters and for effectiveness of chlorine as a bactericide.

Corrosive damage to pipes, filters and pumps might result from operation at a pH below 7.0. High pH values cause reduced effectiveness of bactericides and encourage the growth of algae.

| Increasingly Acid |   |   |   |   | Neutral |   |   | Increasingly Basic |   |    |    |    |    |    |
|-------------------|---|---|---|---|---------|---|---|--------------------|---|----|----|----|----|----|
| 0                 | 1 | 2 | 3 | 4 | 5       | 6 | 7 | 8                  | 9 | 10 | 11 | 12 | 13 | 14 |

| Pool Water Zone  |     |     |  |     |     |   |     |     |
|--|-----|-----|--|-----|-----|---|-----|-----|
| <ul style="list-style-type: none"> <li>○ pH too low</li> <li>○ Corrosive</li> <li>○ Chlorine Lost</li> <li>○ Irritating</li> </ul> |     |     | <ul style="list-style-type: none"> <li>○ pH Ideal</li> <li>○ Neutral</li> <li>○ Maximum Chlorine Efficiency</li> <li>○ Comfort Zone</li> </ul> |     |     | <ul style="list-style-type: none"> <li>○ pH Too High</li> <li>○ Scale Forming</li> <li>○ Chlorine Less Effective</li> <li>○ Irritating</li> </ul> |     |     |
| 6.8  | 7.0 | 7.2 | 7.4  | 7.6 | 7.8 | 8.0   | 8.2 | 8.4 |

Control of pH is relatively simple. pH can be raised by the addition of soda ash (sodium carbonate,  $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ) or sodium sesquicarbonate ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) - Other compounds, such as sodium hydroxide, can be used, but they are more dangerous to handle and are not recommended. The carbonate ions produced by these chemicals combine with some of the hydrogen ions and reduce the hydrogen-ion concentration. This makes the water more basic. Soda ash, sodium

bicarbonate and sodium sesquicarbonate can be added to a pool by dissolving the powder in water and feeding the solution through a chemical feeder; dissolving the powder in a bucket of water and pouring the solution directly into the pool water; or by broadcasting the dry powder over the water surface. The amount required varies greatly from pool to pool, and only trial-and-error experience determines the correct amount for any specific pool.

Addition of acids, or acid salts, causes an increase in hydrogen-ion concentration and lowers the pH. Sodium bisulfate ( $\text{NaHSO}_4$ ) is an acid salt that is frequently used because it is safe to handle. It can be added by chemical feeder or by dissolving in a bucket and pouring directly into the pool. Muriatic acid is the commercial grade of hydrochloric acid ( $\text{HCl}$ ). If the pool operator is sufficiently aware of the dangers and precautions of handling acids, either of these two can be poured directly into the pool when no one is swimming. Acids may also affect the total alkalinity of water. This is discussed in the section on "Control of Total Alkalinity."

The scientific definition of pH is 'the negative logarithm of the Hydrogen ion concentration'.

First accept pH is a scale measuring the acidity or alkalinity of a solution. Squeezed lemon and vinegar are sour or acidic. If we drank them we would take something alkaline like bicarbonate of soda or magnesia to neutralize the acidity in our stomachs - in other words raise the pH. The pH scale runs from 0 (highly acidic) to 14 (highly alkaline) with distilled water being neutral at pH 7.

Now instead of sour, let's use the term 'hydrogen ions', and instead of alkaline let's use the term 'hydroxyl ions'. Vinegar has many more hydrogen ions than hydroxyl ions. Conversely, soda ash and bicarbonate, being alkaline, possess more hydroxyl ions than hydrogen ions. In summary, acids produce hydrogen ions, alkalis produce hydroxyl ions. pH is the power (German 'potenz') of a solution to yield hydrogen ions  $[\text{H}^+]$ .

One more step to go. The scale between 0 and 14 is logarithmic (pH 8 is 10 times more alkaline than pH 7 and pH 9 is 100 times more alkaline than pH 7)

Now we are back to the scientific explanation of pH as 'the negative logarithm of the hydrogen ion concentration'. Negative because the more hydrogen ions, the lower the pH.

**Why is pH so important?**

1. The pH value affects the amount of hypochlorous acid (free available chlorine) that is formed, and therefore determines the effectiveness of the chlorine as a killer of bugs.

At pH 6.5, 90% of the chlorine will be hypochlorous acid

At pH 7.5, 50% of the chlorine will be hypochlorous acid

At pH 8.0, 20% of the chlorine will be hypochlorous acid

Unfortunately you cannot run your pool at pH 6.5 - it would be acidic enough to corrode the metal fittings in your pool circulation system and it is too far from the human body's pH of 7.4 to be comfortable to bathe in. The compromise is 7.2 to 7.6, preferably midpoint of 7.4. Remember, if you let the pH drift out of this range, you will have to use more chlorine to get adequate disinfection.

2. Bather comfort. At high pH, the water will make your eyes sting and possibly give you a sore throat
3. At high pH there are two dangers.
  - a. The danger of scale forming on your pool surfaces, pipe work and fittings. This is because at a pH of around 8.0, the calcium in the water combines with carbonates in the water. Result? Calcium carbonate or scale.
  - b. Calcium carbonate can form into tiny particles and float around in the water giving it a cloudy, turbid appearance.
4. A low pH can corrode metals, eating away at copper fittings and heat exchangers leaving metal oxides to stain pool surfaces. Under certain conditions the precipitated (particulate) metals can tint your hair, giving you a rather dated appearance in these post-punk times!

A final note: Before adding any chemicals to adjust your pH levels, you must first consider total alkalinity.

## **Total Alkalinity**

Is a pH "stabilizer". It helps to keep the pH within the proper levels so that the chlorine can work effectively. It reduces pH "bounce". The level should be between 100 - 150.

Now that you know where your pH level should be, it's time to consider the total alkalinity.

The most important thing to remember about total alkalinity is that it affects your pH levels and therefore must be tested before you do any pH testing and adjustments.

Total alkalinity and pH go hand in hand, but total alkalinity has the upper hand.

Basically, total alkalinity is a measure of the water's ability to neutralize acid (called the water's buffering capacity), and keep your pH level within the proper range. This is why you test and adjust your total alkalinity before even touching your pH test kit.

Your goal? To keep total alkalinity readings inside the acceptable range of 80 to 140 ppm for pools and 80 to 120 ppm for spas.

| What happens if you don't?<br>Let's take a quick look at the<br>problems that can result. <b>High<br/>Total Alkalinity</b> | <b>Low Total Alkalinity</b>  |
|--|--|
| Hard to change pH<br>Scale formation<br>Cloudy water<br>Skin and eye irritation<br>Poor sanitizer efficiency               | Rapid changes in pH or "pH bounce"<br>Stained, etched or dissolved plaster<br>Corroded metals/equipment<br>Skin and eye irritation |

## WHAT IS TOTAL ALKALINITY?

Closely related to pH, but the two must not be confused. Total alkalinity is a measure of the amount of alkaline materials in the water. This alkalinity will usually be present as bicarbonates, but with a very high pH carbonates and hydroxides can be present as well.

The relevance to pH is that the amount of alkali (hardness) in the water will determine how easy it is for changes in pH to occur.

If the alkalinity is too low (below 80ppm) there can be rapid fluctuations in pH - i.e. there is insufficient 'buffer' to the pH. High alkalinity (above 200ppm) will result in the water being too buffered - it will make it difficult to adjust or correct the pH.

By way of analogy, picture a sphere resting on a flat surface. If the sphere moves along the surface to the left, it is analogous to lowering the pH; if it moves to the right, it is equivalent to raising the pH. If the sphere had the bulk density of a balloon, very little force would be required to move it left or right. It would require a much greater force if the sphere had the bulk density of a cannon ball. In this example, the increase in bulk density between the balloon and the cannon ball is analogous to an increase in alkalinity. The increase in force required to move the balloon and the cannon ball is analogous to the idea of increased 'buffering'.

*Total alkalinity* is a measure of the pH-buffering capacity, or the water's resistance to a change in pH. This ability to resist change in pH is due primarily to the presence of the family of carbonate ions, but certain other compounds also provide buffering.

The carbonate ions have a special role in water saturation. The operator must control both the amount of carbonate alkalinity and the pH to provide enough calcium carbonate to saturate the water without having so much that scale forms.

*Total alkalinity and pH* are related in water saturation (or balance) because, at low-pH (acidic) conditions, all of the carbonate ions are converted to bicarbonates. There is no calcium carbonate formed, and water becomes aggressive to the pool walls and equipment. At high-pH (basic) conditions, too much carbonate is formed, and even the smallest amount of calcium ion present precipitates, causing cloudy water or scale. At normal pool pH conditions (7.2-7.6), most of the carbonate ions are in the bicarbonate form to provide buffering. Small amounts of carbonate ion are present to provide calcium carbonate saturation.

Total alkalinity is measured with a pool test kit, and, for all practical purposes, is equal to the carbonate alkalinity. Total alkalinity may be used directly to get the alkalinity factor (AF) for the Langelier Index.

A possible exception is when the total alkalinity of the pool water is *less than* 80 ppm and the cyanuric-acid (chlorine stabilizer) level is *over* 60 ppm. If both these conditions exist, the operator should determine the carbonate alkalinity (CA) by subtracting one-third of the cyanuric acid (stabilizer) level from the total alkalinity. If, for example, the operator finds a total alkalinity (TA) level of 75 ppm and a stabilizer or cyanuric acid (CYA) level of 90 ppm, before calculating the saturation index the following correction should be performed:

Carbonate alkalinity = Total alkalinity - 1/3 Cyanuric acid

or:  $CA = TA - 1/3 \text{ CYA}$

Carbonate alkalinity = 75 ppm - 90 ppm / 3 = 45 ppm

The alkalinity factor from the Langelier Table or Saturation Index Table will be 1.7 (at 45 ppm) not 1.9 (at 75 ppm). If these conditions existed for pool #2 in the examples given earlier, the water would be very aggressive (SI = -0.5 instead of the -0.3 shown), and the operator should take corrective action immediately to avoid corrosion damage to the pool and equipment.

At normal-to-high total alkalinity, there should be no need for a correction, and the total alkalinity test result can be used both as a measure of the pH buffering and the carbonate alkalinity in determining the degree of saturation.

## **Water Hardness**

Water hardness is a concentration of the calcium and magnesium in your pool and spa water but is often referred to simply as calcium hardness.

The amount of calcium hardness your water will have varies depending on your water source. Well water, for example, has a higher mineral content -- or is harder -- than a fresh-water source that has gone through a treatment plant.

Note: You do want your water to have some level of hardness. If it's too soft, the water will slowly but surely dissolve the plaster and any metal in your pool and spa equipment.

If there's too much hardness, you'll see scale formation on the walls and the water will take on a cloudy appearance.

## **WHAT IS CALCIUM HARDNESS?**

Calcium hardness is the amount of dissolved calcium (plus some other minerals like magnesium) in the water. The word dissolved is important - if you can see calcium scaling up the pipe work or the surface of the pool, it is no longer dissolved - it has stolen a march on you. Too much calcium means cloudiness and scaling up, too little could lead to the water satisfying its appetite for calcium by taking it from your grouting.

### **Understanding Calcium Hardness**

The term "water hardness" originated with the use of soap for laundering and cleaning. Certain ions in water combined with the chemicals in soap to form a solid precipitate, or scum, and made it hard to get soap to lather. Thus, water with more than 100 ppm of hardness ions was called *hard water*. The hardness ions are primarily calcium and magnesium. Sometimes, such others as iron and aluminum are also included but are often neglected because they are easily removed in the water-treatment process. With the development of detergents, the problem of hard water in laundering was greatly reduced, but the term is still commonly used.

Because calcium ions combine with carbonate ions to form the calcium carbonate needed for water saturation, it is important that the calcium level be closely monitored. Therefore, the pool operator needs to measure the calcium hardness to determine the calcium factor (CF) for the Langelier Index. The method for determining calcium hardness is given in the chapter on pool water testing.

Like pH and alkalinity, calcium hardness affects the tendency of water to be corrosive or scale forming. It also appears to affect the kind of scale formed. When a calcium carbonate precipitate occurs in soft water, the scale particles are large and coarse. This is seen in many tap water pipes where the local water treatment plants soften the water to 100 ppm or less.

Hard water, however, appears to produce a protective scale that has smaller, finer particles that prevent corrosion. Thus, the pool operator should test and maintain calcium hardness at 200 ppm, or higher, both to provide sufficient calcium ion for saturation as calcium carbonate (50 ppm minimum) and to ensure that, if a scale forms at all, it is the less harmful form (200 ppm or more).

The acceptable maximum calcium hardness depends on the amount of total alkalinity needed for pH buffering. If a particular pool tends to change pH rapidly, higher total alkalinity (over 100 ppm) is needed. Calcium hardness should not exceed 400-600 ppm, depending on the pH and temperature of the water. The exact values can be calculated using the Langelier Index.

Some pools tend to have very little pH drift and can use a lower total alkalinity (less than 100 ppm). Under these conditions, calcium hardness may reach 800 ppm, or more, without causing cloudy water or scale formation. Again, all of the factors for water saturation must be considered in determining the proper level to maintain.

### **Controlling Calcium Hardness**

Calcium hardness is increased by the addition of hydrated calcium chloride, a readily available form of calcium salt. Use 10 pounds of calcium chloride (80% CaCl<sub>2</sub>) for each 10,000 gallons of water to raise the calcium hardness 80 ppm.

The only convenient way to reduce calcium hardness, however, is to remove some of the pool water and replace it with fresh water. Very often, normal splash-out by swimmers and filter backwash procedures remove enough water to maintain an acceptable calcium level. With high temperatures and excessive evaporation rates, additional water may have to be drained periodically to lower calcium hardness levels.

### **Total Dissolved Solids (TDS)**

By definition, TDS is absolutely everything dissolved in your pool and spa water, from metals to chlorine to alkalinity to sulfates and salts. The acceptable range of TDS in a swimming pool is between 1,000 and 2,000 ppm. For spas, the level is 1,500 ppm above your start-up TDS.

If you have a problem with TDS, your pool or spa water may taste salty or it may have a tint to it, although there isn't any clouding. You might also see algae growth and get false test readings, among other things.

If you suspect your water's TDS is too high or low, call a professional service technician or take a water sample to your pool/spa supply store's water lab for further tests -- and some advice.

### **Numbers Game**

By now, you should have read the basic definitions of the different chemicals and substances found in your pool and spa water. And while keeping the upper hand on them doesn't require a Ph.D. in chemistry, it does call for regular attention.

Your ultimate goal is to reach and maintain a certain level of sanitizer and a certain water balance. That is, you want to keep all your chemical readings within their proper ranges.

Here's a quick rundown of the numbers:

|                 |   |
|-----------------|---|
| <b>Chlorine</b> | 1.0 - 3.0 ppm in pools, 1.5 - 3.0 ppm in spas |
| <b>Bromine</b>  | 2.0 - 4.0 ppm in pools, 3.0 - 5.0 ppm in spas |



|                               |   |
|-------------------------------|---|
| <b>pH</b>                     | 7.4 - 7.6 in pools, 7.2 - 7.8 in spas                                 |
| <b>Total Alkalinity</b>       | 80 - 140 ppm in pools, 80 – 120 ppm in spas                           |
| <b>Calcium Hardness</b>       | 200 - 400 ppm in pools and spas                                       |
| <b>Total Dissolved Solids</b> | 1,000 - 2,000 ppm in pools, 1,500 ppm above your start-up TDS in spas |

## WHAT IS TOTAL DISSOLVED SOLIDS?

This apparent contradiction in terms refers to conductive chemicals that can accumulate in the pool particularly when the water evaporates, or when the pool is not 'diluted' with sufficient fresh water. You cannot see them because they are dissolved, but this does not stop them corroding metal parts (pumps, pipe work, filters) on account of their conductivity. They are mostly made up of chlorides and sulphates. Chlorides can accumulate with long-term use of sodium hypochlorite. Regular addition of alum based clarifiers (aluminum sulphate) and dry acid (sodium bisulphate) can increase sulphate levels. Periodic backwashing and water replacement are the best ways of controlling TDS

High TDS - at 1,500 ppm above water-supply level - can reduce chlorine efficiency by as much as 50%. High-TDS water tastes salty and offers a dull appearance. High TDS is common with spa water with high bather load, high chemical needs and a relatively small volume of water. Outdoor pools in the Sun Belt area of the United States that experience a high volume loss of water due to evaporation can be plagued with high TDS, especially in shallow pools. Splash-out, carryout and frequent backwashing offer a natural prevention of high TDS because of dilution. TDS can only be corrected by dilution of water with low TDS. Seawater has an approximate TDS of 35,000 ppm, while drinking water can range between 100-300 ppm.

## Stabilizer

Forms a protective bond around the chlorine, making it more resistant to being burned off by the sun. Makes chlorine tablets last longer. Pools should be stabilized whenever large amounts of fresh water are added. The level should be 35 ppm and is adjusted by adding Stabilizer Conditioner. Usually Cyanuric Acid is used as Stabilizer.

## WHAT IS CYANURIC ACID?

Chlorine in outdoor pools must be shielded from the degrading effects of the sun's ultraviolet (UV) rays. Cyanuric acid is used in outdoor pools with the inorganic chlorines such as calcium hypochlorite, sodium hypochlorite, lithium hypochlorite and chlorine gas.

It is recommended that the cyanuric- acid level be 30-50 ppm with a maximum of 100 ppm and a lower limit of 10 ppm. The level of cyanuric acid is reduced by dilution due to filter backwashing, bather dragout or dumping. To meet health codes, pools above 100 ppm need to be drained of about 20% of volume, and fresh water added. Four pounds

of cyanuric-acid will offer a reading of 50 ppm in 10,000 gallons of water. Cyanuric acid has a pH of 4.0, and if added to a gas-chlorinated pool, the addition of one-third of a pound of soda ash per pound of cyanuric acid is recommended.

'Chlorine Lock,' a term given to a condition once thought to be produced from high cyanuric-acid levels tying up free available chlorine, has been proven false by the industry. Generally, high cyanuric-acid levels of 400 ppm or higher are associated with excessive Total Dissolve Solids (TDS) or combined chlorine or chloramines and not 'Chlorine Lock.'

**REMEMBER** - Good water chemistry can only be achieved when all four of chemical levels are kept constant. Good Alkalinity helps keep the pH in the right range so that the chlorine can do its job properly. Stabilizer keeps more of the chlorine in the water instead of being wasted! The result? A crystal clear pool!

## Testing Your Water

The subject of water testing may transport you back to the days when you were in school and final exams were approaching -- all too quickly for your comfort. Rest assured, pool- and spa-water tests are much less painful than you may imagine. What's more, regularly testing your pool and spa water is a critical part of any maintenance routine. Each element defined in the Keeping Your Water Balanced section has a specific test to give you an up-to-the-minute evaluation of your pool and spa water. Once again, your pool/spa supply shop is the best place to buy these test kits. To give you a brief outline of their use, we review all the various tests you -- or your service professional -- must perform on your pool and spa.

## How Much of What Chemical?

This is the science of water treatment. The table below, Chemical Adjustments, is part of the formula. But each pool has its own personality and demands. Only through record keeping and experience can one determine and perform the correct tasks.

|                        | Unit | Minimum | Ideal   | Maximum |
|------------------------|------|---------|---|---------|
| Free Chlorine, ppm     | ppm  | 1.0     | 1.0 - 3.0   | 3.0     |
| Combined Chlorine, ppm | ppm  | None    | None  | 0.2     |
| Bromine, ppm           | ppm  | 2.0     | 2.0 - 4.0   | 4.0     |
| pH                     | No   | 7.2     | 7.4 - 7.6   | 7.8     |
| Total Alkalinity, ppm  |      | 60      | (for liquid chlorine, Cal-Hypo and Lithium Hypo)<br>80 - 100<br>100 - 120 | 180     |

|                  |     |     |   |             |
|------------------|-----|-----|---|-------------|
|                  |     |     | (for Gas Chlorine, Dichlor, Trichlor and Bromine Compounds) |             |
| TDS              | ppm | 300 | 1000 - 2000   | 3000        |
| Calcium Hardness | ppm | 150 | 200 - 400   | 500 - 1000+ |
| Cyanuric Acid    | ppm | 10  | 30 - 50   | 150         |

## Sanitizer/Oxidizer Tests

There are two well-known test kits available to test levels of chlorine and bromine, the DPD and OTO. Each has a long, scientific name, but all you really need to know are the initials. The DPD is the preferred of the two because it tests for free available chlorine -- the most powerful "killing form" of chlorine. Its chemical reagent reacts with the free available chlorine in the sample water to change its color. The ideal range of 1.0 to 3.0 ppm for pools or 1.5 to 3.0 ppm for spas will command a pink to red color. To get an accurate reading, just compare your test sample to the manufacturer's chart that should be included with the test kit.

Note: An extremely high level of chlorine tends to bleach out the test water, making it appear as if there isn't any chlorine present. This would normally prompt you to add more chlorine, and in most cases, that's correct. If you think you have received a false reading, conduct the test again, except this time, fill the test vial with 50 percent chlorine-free or tap water and multiply the results by two. This will help you determine whether you have a low level or very high level of chlorine in your water.

The other, less common, test is the OTO, which works on the same basic principle, but will turn the water yellow to deep orange when chlorine is in the proper range. One of the major differences between the OTO test and the DPD test is that OTO cannot distinguish between total chlorine and free available chlorine. You won't get an accurate estimate of how much killing chlorine is in your pool or spa water. A final note: Bromine can also be tested using either method, but the results need to be multiplied by 2.25 to yield a true reading - - unless, of course, you have one of the test kits that include a bromine color chart as a reference. So far so good? Let's move on to pH.

## pH Readings

The most common pH test for pool and spa owners is the phenol-red test. Just like the DPD and the OTO, the phenol-red test has a reagent that mixes with the acid in the water to cause a color change in the sample. If your pH is in the correct range, the water sample should turn a shade of red ranging from pink to orange. If you get a yellow result, you have a low pH or acidic water. If the color is a deep purple, your pH is too high. Once again, you'll need to compare your results with the color chart provided with the test kit to get an accurate reading.

## TESTING FOR pH VALUES

pH of water is determined by adding a reagent (containing an organic dye) to the sample at a measured rate. Reagents to cover the entire pH range of 1.0 to 14.0 are available. Because most pools are kept in a pH range of 7.2-7.6, the pH test that uses phenol red as a reagent is particularly effective (pH range of 6.8-8.2). Phenol red is available in either liquid or tablet form. To test with phenol red, add one tablet or a specified number of drops of liquid, to the water sample, and compare the resulting color to the test-kit standard. At the low end, the sample is yellow, developing an increasingly red color as the pH increases. At the high end, the color is almost purple.

Some reagents are subject to bleaching by chlorine; others react with the chlorine to form new compounds that can give false readings. Bleaching action should be neutralized by adding a 2-4 drops of chlorine neutralizer (sodium thiosulfate) before the test is performed. (Some indicator solutions sold specifically for pools already contain a chlorine neutralizer to combat this bleaching action.)

### Solution Method for Testing for pH Value

1. Rinse the sample cell in pool water.
2. Fill the sample cell to the marked fill line with pool water.
3. Add 2-4 drops of chlorine neutralizer to remove the chlorine and prevent bleaching. (As mentioned earlier, many test kit manufacturers market pH indicators containing chemicals that eliminate the bleaching effect of chlorine, making this step unnecessary.)
4. Add the prescribed number of drops of phenol red to the sample cell.
5. Cap the sample cell, and mix the contents by inverting several times, or swirl. Do not use a finger in contact with the solution.
6. Compare the color of the sample with the test-kit color standards.

Look for a hue or color comparison, not a color intensity, as in the chlorine test. A shade between two standard color values indicates that the pH is the midpoint between the values assigned.

### Tablet Method for Testing for pH Level

1. Rinse the sample cell in pool water.
2. Fill the sample cell to the marked fill line with pool water.
3. Add one phenol red indicator tablet to the cell. Invert the sample cell to dissolve the tablet.

**CAUTION:** Do not shake the solution vigorously. If the tablet fails to dissolve with gentle agitation, crush it with a clean plastic rod.

After the tablet has dissolved, compare the color with the standards, as above.

Note: The spa's temperature makes a definite impact on the accuracy of this test. Therefore, the test should only be conducted with spa water when its non-operating temperature is between 60 and 80 degrees Fahrenheit. Adjusting pH is a very simple task. If you have a low pH, add soda ash or sodium bicarbonate. If your water's pH is high, add liquid muriatic acid or dry acid. (Remember, both soda ash and muriatic acid are too strong for use in spas.) Before you attempt to change the pH, however, you need to perform a second test to figure out how much of which substance you'll need to add to the water. A base-demand test determines how much soda ash or bicarbonate is required and an acid-demand test calculates how much meiotic or dry acid is needed. These tests are called titration tests or end-point reactions. In this type, the number of drops of a special liquid it takes to cause a color change corresponds with the amount of soda ash or acid required. Consult the test kit manufacturer's recommendations for the exact amounts. One more caution: Before doing anything about your pH levels, you also need to test the total alkalinity of your pool or spa water, as described below.

## **Total Alkalinity Test**

This test -- the last of the regularly performed tests -- measures total alkalinity. As noted above, this test should be done before you do your pH test and adjustments. The two factors are interrelated and must be dealt with together. Total alkalinity is determined by using a titration test with two reagents. The first changes the color of the test sample, the second triggers an end-point reaction. It's with the second test you count the number of drops of reagent added to the water -- swirling the sample after each drop -- until it changes color. Note: This reaction occurs very suddenly so don't add the second reagent too quickly.

## **TESTING FOR TOTAL ALKALINITY**

Take a 100ml pool water sample in a stoppered bottle. Using Palintest Alkalinity M tablets, add one tablet at a time shaking the bottle until dissolved. Keep adding tablets until the color changes from yellow to bright pink. Count the number of tablets used and work out the alkalinity -  $\text{Alkalinity} = (\text{number of tablets} \times 40) - 20 \text{ ppm}$ .

Testing for total alkalinity is essential to make proper determinations of the saturation index as well as for bather comfort and ease of pH control.

A pool's total alkalinity may be determined through use of one of many commercially available test kits. A quantity of pool water is mixed with an indicator; a blue color reveals the presence of alkalinity. A reagent is added to this mixture from a dropper. The operator counts the number of drops necessary to neutralize the alkalinity and bring about a color change. Alkalinity can be determined by multiplying the number of drops used by a constant as provided by the test kit manufacturer (usually 1 drop = 10 ppm).

Tablet methods also are available for determining alkalinity. Although less accurate than the drop counting method, the process is easy to follow and is less susceptible to operator error. Tablets are added one at a time until the desired color change takes

place. When sufficient tablets have been added to bring about the end-point color change, the number of tablets required is multiplied by the constant provided by the test-kit manufacturer.

It is recommended that the results of total alkalinity be considered before adjusting pH. The direction of pH change, or even the need for adding chemicals, is greatly influenced by the level of total alkalinity. Total alkalinity does not vary quickly and often is only tested once a week.

### **Calcium Hardness Levels**

Tests for calcium hardness are performed at the beginning of the swim season, when you start up a new pool or after draining and refilling a pool or spa. After that, they only need to be done every three months or so. But don't forget about it entirely because when allowed to go too high or too low, the water's hardness levels can cause all kinds of problems. (For more on water hardness, see the section on Keeping Your Water Balanced.) Like total alkalinity, an end-point reaction best measures calcium hardness. The first reagent is a pH buffer to bring the pH level up to approximately 10. The second step adds a dye that, when reacting with calcium, turns the sample water a different color. Next, the titrant (EDTA) is added one drop at a time until the water changes color. The total number of drops required gives you the amount of hardness when compared with a manufacturer's chart.

### **TESTING FOR CALCIUM HARDNESS**

Take a 100ml pool water sample in a stoppered bottle. Using Palintest Calcium Hardness tablets, add one tablet at a time shaking the bottle until dissolved. Keep adding tablets until the color changes from pink to bright violet. Count the number of tablets used and work out the hardness - *Hardness = (number of tablets x 20) - 10 ppm*.

Taking 70% of the total hardness level can approximate calcium hardness in a freshly filled pool. However, more accurate measurements can be made by using a test kit designed specifically to determine calcium hardness and by following the manufacturer's directions regarding color changes.

In these tests, a specific amount of water is taken from the pool, and an indicator is added to the sample. A reagent is added, causing a color change that indicates the calcium hardness level in ppm.

### **Total Hardness**

### **TESTING FOR TOTAL HARDNESS**

To test for total hardness, an exact amount of pool water (usually 60 ml) is treated with a solution called a buffer. Then a dye is added. The reagent is added to the sample and

mixed, one drop at a time. The number of drops necessary to change the water color, multiplied by a constant provided by the manufacturer, determines the hardness in ppm.

The tablet method for testing water hardness is equally simple. A tablet containing the pH buffer, the indicator dye, and the hardness reagent is added to a 100 ml sample of water. The color changes as additional tablets are added. The number of tablets required to bring about this change is recorded and multiplied by a constant provided by the test-kit manufacturer.

## **Total Dissolved Solids**

### **TESTING FOR TOTAL DISSOLVED SOLIDS**

Total dissolved solids (TDS) is the measurement of all materials dissolved in the water, i.e., calcium, carbonates, dissolved organic and inorganic materials, salts from chlorine residue, swimmer waste, soluble hair and body lotion or anything placed in the pool that can be dissolved.

TDS is measured by using a portable electronic analyzer. The equipment is specifically used to measure for dissolved solids and should be standard equipment for operation of spas and hot-water pools. A pool should be dumped and refilled when a TDS reading exceeds 1,500 ppm above the domestic water supply reading. This equipment is quite expensive and is not normally at the disposal of the private pool owner, so you have two choices:

1. Take your sample of pool water to your pool center and ask them to measure TDS for you. They will normally be happy to do this for you free of charge if you usually buy your chemicals etc from them.
2. As TDS plays a less important part in the calculation than the other factors you can estimate it, but do bear in mind that this will then only give you a rough idea of whether the water is scale forming or corrosive. As a guide, for pools, which have been recently refilled, use a figure of 750ppm. For pools which have not been recently refilled, or where there has been little water replacement by backwashing, or where cyanuric acid levels are above 200ppm, use a figure of 1500ppm for TDS.

## **Super Chlorination or Shocking**

Super chlorination is a term that describes an extra large dose (usually 8 to 10 ppm) of chlorine to oxidize organic compounds and kill and remove algae and other contaminants from the water. This is the same as using three to six times the normal dosage of a chlorinating agent. For example, a 50,000-gallon pool requires about four gallons of liquid pool chlorine (12% Available Chlorine) or six pounds of a granular chlorinating compound such as calcium hypochlorite (65% Available Chlorine).

As mentioned, HOCl is the form of chlorine that provides sanitation. Because it is an extremely active chemical, however, it also reacts with organic impurities. When there is enough HOCl present, the impurities are completely oxidized. Combined chlorine is formed when there is an insufficient supply of HOCl or when there is a very high level of organic impurities. Combined chlorine compounds can be oxidized by increasing the HOCl level in the water. The point at which all the organic impurities are oxidized is called the breakpoint. The addition of sufficient chlorine to reach this point is known as breakpoint chlorination.

Every once in a while, your pool or spa water may become a veritable hotel of unwelcome contaminants and bather waste products. You can often detect when this happens because a "chlorine" odor may begin emanating from your pool or spa, or you may notice that you're experiencing some skin and eye irritation. But the most reliable -- and better -- way to monitor your water quality is to take a second look at your sanitizer readings. If your chlorine test readings keep dropping hard and fast, you may be faced with the need to evict chloramines from the water. (For more on how chloramines form, see the section on Keeping Your Water Balanced.) This is done easily enough with a process called shocking. No, you don't electrocute the chloramines. What this process entails is adding extra high doses of sanitizers to the water. By adding a large dose of chlorine -- a process called super chlorination or shocking -- you bring up your residual of free available sanitizer in a relatively short period of time. The newly added sanitizer will promptly rid your pool and spa water of those annoying guests. To be safe, do not use your pool or spa for at least 24 hours after shocking with chlorine. You should also test for the proper sanitizer levels before getting back in the water.

Note: There are non-chlorine shocking products available that lessen the amount of time swimmers need to stay out of the pool or spa. Check with your local pool/spa supply store or professional service technician for more information.

## **Adding Chemicals to Water**

1. Add large amounts gradually in thirds over a 2-hour period.
2. Add directly into the pool or spa when no swimmers are present and time is sufficient to permit even distribution of the chemicals
3. Add indirectly in small amounts slowly through skimmer or overflow to prevent corrosion of metals
4. Add chemicals through feeders or feeder lines that follow pump and filters, especially DE filters.
5. Add granular chlorine or soda ash solution directly to the pool, but separately. Always mix chemicals into plastic containers that have been filled with water first.
6. Add chemicals evenly by walking the perimeter of the pool.
7. Add chemicals to achieve maximum for Free Available Chlorine, FAC (3.0 ppm) and minimum pH (7.4) parameters in anticipation of a heavy bather load. This is an effort prevent falling below minimum standards in FAC during or following the loading period.



8. Add chemicals frequently to prevent highs and lows in readings. Large reading fluctuations are hard on soft metals and produces a bounce effect on water treatment.
9. Add additional chemicals only following an adequate time period that permits a second or third chemical reading.
10. Add chemicals in sequence to adjust for (1) FAC, (2) Total Alkalinity, (3) pH, (4) Cyanuric Acid and (5) Total Hardness.
11. An effort should be made to offer adequate time for chemical distribution and most importantly, a second reading before leaving the scene. Screen test for pH, FAC and combined chlorine first, and if pH is extreme, test for total alkalinity. Test for balance or saturation, TDS and metals can be decided based on the history of the pool.

## Glossary of Terms

The following is a glossary of terms to help you develop your water chemistry vocabulary.

|                             |   |
|-----------------------------|---|
| <b>Bromine</b>              | A chemical that works as a sanitizer or disinfectant to kill bacteria and algae in pool and spa water. This chemical does not eliminate swimmer waste unless it is combined with an oxidizer. It is very susceptible to direct sunlight, therefore is not efficient in outdoor pools. The ideal range is from 2.0 to 4.0 ppm for pools and 3.0 - 5.0 ppm in spas. |
| <b>Calcium hardness</b>     | The amount of calcium and magnesium in pool and spa water. The ideal range is from 200 to 400 ppm in both pools and spas.   |
| <b>Calcium hypochlorite</b> | A common type of chlorine used in pools and spas. A granular or tablet substance typically dissolved in water prior to adding it to the pool and spa water.   |
| <b>Chloramines</b>          | An inefficient disinfectant formed when chlorine has combined with ammonia and nitrogen in pool and spa water. It exudes a foul, "chlorine" odor and causes skin and eye irritation.  |
| <b>Chlorine</b>             | A chemical that works as a sanitizer or disinfectant in pool and spa water to kill bacteria and algae, and oxidizes ammonia and nitrogen compounds such as swimmer waste. The ideal range is from 1.0 to 3.0 ppm in pools and 1.5 - 3.0 ppm in spas.  |
| <b>Chlorine gas</b>         | This is the most pure form of chlorine and can only be applied to pools by a trained professional. It is not an appropriate sanitizer for spas.   |
| <b>Colorimetric tests</b>   | A test for chlorine, bromine and pH where the reagent causes a change in color when reacting with the specified chemical.   |
| <b>Cyanuric acid</b>        | A stabilizer that works to keep a reserve of "free available" chlorine in   |

|                                |  |
|--------------------------------|--|
|                                | pool and spa water, protecting it from direct sunlight. Because their exposure to sunlight is limited, it is not frequently used in spas. It is, however, present in some sanitizers such as trichlor and dichlor. The ideal level is from 30 to 100 ppm in both pools and spas. |
| <b>DPD</b>                     | A common chlorine or bromine test using color change as an indicator. It allows for separate free available and combined chlorine testing.   |
| <b>End-point reaction</b>      | The resulting color change in a test sample created when you add drops of a given reagent. The number of drops correlates with a measurement.  |
| <b>Free available chlorine</b> | The killing, active form of chlorine.  |
| <b>Lithium hypochlorite</b>    | A granular form of chlorine used in pools and spas. It is known for its tendency to dissolve quickly.  |
| <b>Muriatic acid</b>           | A liquid acid that is most commonly used to reduce pH and total alkalinity levels. It tends to be very strong, and is not recommended for use in spas.   |
| <b>OTO</b>                     | A common chlorine or bromine test using color change as an indicator. This test will not separate free available chlorine from combined chlorine.  |
| <b>Ozone</b>                   | A powerful gas that acts as a sanitizer and oxidizer, but is highly unstable and cannot be used to create a sanitizer residual.  |
| <b>Parts per million (ppm)</b> | A unit of measurement used for chlorine, bromine, total alkalinity, calcium hardness and total dissolved solids.   |
| <b>pH</b>                      | A level determining the acidic or basic quality of pool and spa water. The ideal range is from 7.4 to 7.6 in pools and 7.2 to 7.8 in spas.   |
| <b>Phenol red</b>              | A common pH test that uses color change as an indicator.   |
| <b>Scale formation</b>         | This usually occurs on the walls of the pool or spa when there are high levels of calcium hardness, total dissolved solids, pH and total alkalinity.   |
| <b>Shocking</b>                | Adding a large dose of chlorine or other chemical's to quickly increase the amount of free available sanitizers compared with the less effective, "combined" form of the sanitizer.  |
| <b>Soda ash</b>                | A substance used to raise pH and total alkalinity. It is not recommended for use in spas.  |
| <b>Sodium bicarbonate</b>      | Otherwise known as household baking soda, this substance is used to raise pH and total alkalinity levels in pools and spas.  |
| <b>Sodium</b>                  | Otherwise known as common household bleach, this is the most   |

|                               |   |
|-------------------------------|---|
| <b>hypochlorite</b>           | common form of liquid chlorine used in pools and spas.  |
| <b>Test strips</b>            | Chemically treated strips that have the appropriate amounts of reagents on them. Simply dip them into the water and read the reactions. These strips can test free available and total chlorine, bromine, pH, calcium hardness, total alkalinity and cyanuric acid. |
| <b>Titration test</b>         | A test used for acid and base demands, total alkalinity and calcium hardness. It creates an end-point reaction by adding drops of the reagent to elicit a change in the sample's color. The number of drops required correlates with the measurement.               |
| <b>Total alkalinity</b>       | Works in a buffering capacity, protecting the water from dramatic pH changes. The ideal range is from 80 to 140 ppm in pools and 80 to 120 ppm in spas.   |
| <b>Total dissolved solids</b> | The total amount of dissolved materials in pool or spa water. The ideal range is from 1,000 to 2,000 ppm in pools and 1,500 ppm above the start-up TDS in spas.   |
| <b>Turbidity tests</b>        | Used to test the amount of cyanuric acid in the water. The reagent causes a cloudiness of the test water. Measurement is obtained by comparing the test water's visibility (the degree of clarity of a dot in the test vial) to the test kit manufacturer's chart.  |
| <b>Water balance</b>          | This balance is reached when all elements (pH, total alkalinity, calcium hardness and total dissolved solids) are within their proper ranges.   |

## Troubleshooting Guide

Here's a quick troubleshooting guide to a variety of problems you may face with your pool and spa water. You can use this reference to help identify and solve common problems. But, as always, don't hesitate to check with your local pool/spa retailer, supplier or service technician for any help you need bringing your water back in line. The next section explains the pool and spa troubleshooting.

### Pool

| <b>Problems</b>     | <b>Possible Causes</b> | <b>Solutions</b>  |
|---------------------|------------------------|---|
| <b>Algae growth</b> | Low sanitizer levels   | Shock the water. Brush the pool walls. Run the filter for a 24-hour period to increase distribution of sanitizer. Add an algaecide. |

|                                  |  |  |
|----------------------------------|--|--|
| <b>Cloudy water</b>              | High calcium hardness levels<br>High total alkalinity levels<br>High pH levels<br>High TDS levels<br>Algae growth<br>Low sanitizer levels<br>Rain<br>High swimmer load<br>Pets | Test all chemical levels and make the appropriate adjustments.   |
| <b>Colored water</b>             | For green or blue green high pH levels<br>For brown to red-overall water imbalance   | For green or blue green-Test the pH level and make the appropriate adjustments.<br>For brown to red-Test pH, total alkalinity and calcium hardness levels. If necessary, drain all or part of the water and refill with fresh water. |
| <b>Corrosion</b>                 | Low pH levels<br>Low total alkalinity levels   | Test pH and total alkalinity levels, make appropriate adjustments and consult a professional service technician or your pool supply store for more information.  |
| <b>Etched plaster</b>            | Low pH levels<br>Low total alkalinity levels   | Test pH and total alkalinity levels, appropriate adjustments and consult a professional service technician or your pool supply store for more information  |
| <b>pH bounce</b>                 | Low total alkalinity levels  | Test total alkalinity levels and make the appropriate adjustments.   |
| <b>pH resistance</b>             | High total alkalinity levels   | Test total alkalinity levels and make the appropriate adjustments  |
| <b>Poor sanitizer efficiency</b> | High pH levels<br>High total alkalinity levels   | Test pH and total alkalinity levels and make the appropriate adjustments.  |
| <b>Scale formation</b>           | High pH levels<br>High total alkalinity levels<br>High TDS levels<br>High calcium hardness levels  | Test pH and total alkalinity levels and make the appropriate adjustments. If necessary, have a pool professional drain the pool, scrub down the walls and refill with fresh water.   |
| <b>Skin and eye irritation</b>   | Low or high pH levels<br>Low or high total alkalinity levels<br>Low sanitizer levels   | Test pH and total alkalinity levels and make the appropriate adjustments. Sanitizer levels and, if extremely low, shock the pool water.  |

|               |   |  |
|---------------|---|--|
| <b>Stains</b> | Low pH levels<br>Low total alkalinity levels<br>High TDS levels | Test pH and total levels and make the appropriate adjustments. If necessary, have a professional drain the pool, scrub down the walls and refill with fresh water. Consult with a professional service technician or a pool retailer for more information. |
|---------------|---|--|

## Spa

| <b>Problems</b>       | <b>Possible Causes</b>   | <b>Solutions</b>   |
|-----------------------|--|--|
| <b>Algae growth</b>   | Low sanitizer levels   | Shock the water. Brush the spa walls. Run the filter for a 24-hour period to increase distribution of sanitizer. Add an algaecide  |
| <b>Cloudy water</b>   | High calcium hardness levels<br>High total alkalinity levels<br>High pH levels<br>High TDS levels<br>Algae growth<br>Low sanitizer levels<br>Rain<br>High swimmer load<br>Pets | Test all chemical levels and make the appropriate adjustments.   |
| <b>Colored water</b>  | For green or blue green-<br>high pH levels<br>For brown to red-overall<br>water imbalance  | For green or blue green- test the pH level and make the appropriate adjustments.<br>For brown to red- test pH, total alkalinity and calcium hardness levels. If necessary, drain all or part of the water and refill with fresh water. |
| <b>Corrosion</b>      | Low pH levels<br>Low total alkalinity levels   | Test pH and total alkalinity levels, make appropriate adjustments and consult a professional service technician or your spa supply store for more information.   |
| <b>Etched plaster</b> | Low pH levels<br>Low total alkalinity levels   | Test pH and total alkalinity levels, make appropriate adjustments and consult a professional service technician or your spa supply store for more information.   |

|                                  |   |   |
|----------------------------------|---|---|
| <b>Foaming</b>                   | A buildup of organic dirt, soaps, shampoos and oils   | Drain and clean the spa and spa filter.   |
| <b>pH bounce</b>                 | Low total alkalinity levels   | Test total alkalinity levels and make the appropriate adjustments.  |
| <b>pH resistance</b>             | High total alkalinity levels  | Test total alkalinity levels and make the appropriate adjustments.  |
| <b>Poor sanitizer efficiency</b> | High pH levels<br>High total alkalinity levels  | Test pH and total alkalinity levels and make the appropriate adjustments.   |
| <b>Scale formation</b>           | High pH levels<br>High total alkalinity levels<br>High TDS levels<br>High calcium hardness levels | Test pH and total alkalinity levels and make the appropriate adjustments. If necessary, drain the spa, scrub down the walls and refill with fresh water.  |
| <b>Skin and eye irritation</b>   | Low or high pH levels<br>Low or high total alkalinity levels<br>Low sanitizer levels              | Test pH and total alkalinity levels and make the appropriate adjustments. Test sanitizer levels and, if extremely low, shock the spa water.   |
| <b>Stains</b>                    | Low pH levels<br>Low total alkalinity levels<br>High TDS levels                                   | Test pH and total alkalinity levels and make the appropriate adjustments. If necessary, drain the spa, scrub down the walls and refill with fresh water. Consult with a professional service technician or a spa retailer for more information. |

## Advanced Pool and Spa Water Chemistry

The next section describes the Advanced Pool and Spa Water Chemistry procedures to keep clean and balanced water.

### Pool Treatment - It's Not Purely Physical

Because a swimming pool system begins as a hole in the ground, without any water movement, it is an artificial structure. Consequently, it lacks the three purifiers that protect water quality in natural bodies of water:

1. Aeration - This is the addition of oxygen to the water, and results from the continual flow of water through lakes, streams and rivers.

2. Dilution of sediment - This is exactly what it sounds like, and also results from continual water flow.
3. Prevention of contaminant buildup - This happens when water flow causes movement and dilution, while aquatic organisms contribute to a process of biodegradation.

Since any pool lacks these purifiers, it's subject to rapid stagnation. In addition, it's also generally contaminated with bacteria, algae, and organic materials from swimmers wastes. (Did you know that an active bather produces up to two pints of perspiration per hour?) Add dust and dirt, and you get plenty of ways for a pool to go bad.

The world's fanciest physical treatment facilities alone won't keep a pool from getting gunked up. So let's look at the obvious: a swimming pool must be disinfected.

These disinfectants must remove bacteria, algae and organic contaminants. They have to improve water clarity and color. And they have to work together as a total system, so everything functions well.

Enter the hero. Namely, chemicals. More specifically, chlorine. Most pools in the U.S. use it in one form or another.

Why? Well, when chlorine compounds are dissolved in water, hypochlorous acid is formed. (Remember that name-it does the actual sanitizing.)

In most cases, the non-chlorine part of the chlorine compound serves no other purpose than to hold the chlorine until the product dissolves. You'll notice we said in most cases.

Lets get more specific. There are three categories of sanitizers:

1. Chlorine gas at 100% available chlorine.
2. Inorganic hypochlorites such as calcium hypochlorite(now marketed at 65% available chlorine) and sodium hypochlorite (liquid bleach, at 10-15% available chlorine).
3. And finally, the chlorinated isocyanurates like granular (at 56% available chlorine) and tablets (at 90% available chlorine).

Secondary chemical treatment with substances that control pH and buffer the pool is also needed for healthful swimming. Depending on pool conditions, secondary treatment might include decolorizers, additional algaecide, and chemicals to adjust mineral levels (hardness) or retard evaporation.

### **What You Use is What You Get**

We can begin by saying that all three sanitizers are compatible and effective with other chemicals in pool water. (Let's be fair.) Each will perform its function without causing objectionable tastes, odors or colors in the water - if properly applied.

1. CHLORINE GAS... reacts with water to form hypochlorous acid, the active sanitizing species, plus hydrogen ion ( $H^+$ ) and chloride ion ( $Cl^-$ ). Hypochlorous acid exists in a pH dependent equilibrium with hypochlorite ion ( $OCl^-$ ) in pool water.

Now let's look at the nuts - and - bolts. Chlorine's major advantage is its relative low cost. Many large pools and most bulk drinking and wastewater treatment systems use it for this reason.

Chlorine also has several disadvantages. It's a gas that must be delivered in bulky metal cylinders. It has to be applied to the water through sophisticated metering systems operated by trained personnel. And it's highly corrosive, toxic, and very acidic - due to the  $H^+$  and  $Cl^-$  (muriatic acid), the byproduct of its reaction with water.

Most regulated pools are required to install separate feeding equipment to add approximately 1.25 pounds of soda ash to neutralize the acidity of one pound of chlorine gas.

If chlorine gas were the only chemical available to disinfect water, it's very likely that there would be no home swimming pools. Probably no swimming pool industry, either. The complexities and the hazards of this chemical are simply beyond the capabilities of the average pool owner.

Fortunately, more convenient methods of chlorinating pool water have been developed. We move on.

2. THE INORGANIC HYPOCHLORITES... also react with pool water to produce hypochlorous acid, the major disinfectant in chlorine. The hypochlorites are available as the granular calcium hypochlorite (@65% av.  $Cl_2$ ) and liquid sodium hypochlorite ( $NaOCl$ ) (@ 9-15% av.  $Cl_2$ )

Both forms can easily be added in the proper dosage for virtually any size pool. They're relatively inexpensive. However, both forms have a high pH, and may require frequent additions of acid to maintain pool water in the proper pH range for chlorine efficiency, equipment longevity and bather comfort. Otherwise they tend to eat up pools... a big problem.

Calcium hypochlorite, with a pH of 10-12, also contains 5-8% of insoluble material, which can cause cloudy water. A by-product of this reaction is the calcium ion ( $Ca^{++}$ ), a major component of water hardness, and a contributor to scaling tendencies in the pool.

Sodium hypochlorite, with a pH of 12-14 is relatively low in available chlorine concentration. Therefore, more is required to maintain the disinfectant residual in a pool. Because of the bulk of its liquid form and its poor storage stability, it must



be purchased frequently throughout the pool season. Although it does not add hardness to the pool, its high pH can contribute to scaling tendencies in hard water areas.

Neither product provides protection against the destructive effects of sunlight on a chlorine residual. That's why more frequent chemical additions and adjustments are necessary to maintain satisfactory water quality.

And so, friends, we move on to number three.

3. THE POOL CHLORINATING CONCENTRATES... provide the effectiveness of HOCl, the ease and convenience of concentrated solids, and the benefits of stabilization, to provide outstanding water quality with minimum effort and expense. In case you didn't know. Actually, granular reacts with water to produce the same active sanitizing species, hypochlorous acid. Therefore, it is an effective bactericide and algicide that will oxidize organic contaminants. Tablets react similarly, but produce three units of hypochlorous acid.

Both the granular and tablets have a by-product known as cyanuric acid (remember that name!) which is the only known chemical that stabilizes a free chlorine residual without interfering with its sanitizing effectiveness. (Don't panic, we'll talk about free chlorine later. Suffice it is to say that free chlorine is the amount of chlorine available to do its job of sanitizing the water.)

A look at the physical and chemical properties of the pool chlorinating concentrates will help to explain their advantages.

Both the granular and the tablets are based on cyanuric acid, the central structure composed of alternating carbon and nitrogen atoms.

- In the granular two atoms of chlorine are added, giving an available chlorine of 56%. Because this is a sodium salt, it has excellent solubility @ 26.1% and a nearly neutral pH of 6.7. It may be added directly to the pool by hand broadcasting. Or, it can be pre-dissolved and added as a hypochlorinator solution.
- The tablet contains three atoms of chlorine, giving it 90% av. Cl. It has a relatively low pH of 2 -3. Because of its high available chlorine content, much less needs to be added. So it, too, has a minimal impact on pH. Its low solubility of 1.2% makes it an ideal candidate for tabletting and use in continuous feeding systems.

We strongly recommend that this trichloro product not be added directly to the pool in either its tableted or granular form. Its high available chlorine, slow solubility and acidic pH give it the potential to bleach, etch or pit any pool surfaces that it contacts.

Both products are free of insoluble residues, produce a minimal impact on pH and do not contribute to water hardness or scaling. After the chlorine has been consumed in performing the sanitizing functions, the cyanuric acid remains dissolved in the water to provide maximum stabilization for the free chlorine residual.

Exactly what is chlorine residual? Good question.

When chlorine is added to water in a newly filled pool, some of it is consumed in the process of destroying algae, bacteria and other oxidizable material in the water.

The amount of chlorine consumed in this process is referred to as the chlorine demand of the water.

Once the chlorine demand is satisfied, any additional chlorine added is referred to as chlorine residual. Not too complicated, eh?

Two types of chlorine residual can exist:

1. Free chlorine residual-this is a chlorine available to do its job of sanitizing the water.
2. Combined chlorine residual-this is chlorine combined with simple nitrogen compounds such as ammonia and urea. This chlorine (or chloramine) is non-effective as a sanitizer compared to free available chlorine.

It's essential to maintain a free-chlorine residual at all times to achieve sparkling clear, sanitary pool water. This is accomplished by periodic superchlorination of the pool water. (More on that later). Superchlorination consists of simply adding a larger than normal dosage of chlorine to burn out nitrogenous materials.

When chloramines are removed, better efficiency of chlorine is achieved. More of the chlorine residual can then exist as the free or active form, rather than as the less effective combined form.

All right, we've talked about stabilization. What is it? Also a good question.

By now, you should know that cyanuric acid reduces chlorine consumption. The benefits of using it for stabilization have been established and repeatedly verified since the concept was patented by FMC Corp. That's right patented! The biggest problem with chlorine is that it breaks down and dissipates very easily under the sun's radiation. In 1958, FMC Corp. conceived, developed and patented a way of stabilizing pool chlorine by using cyanuric acid. Numerous field tests and evaluations have demonstrated that the addition of a minimum of 30 parts per million of cyanuric acid to swimming pool water prevents wasteful destruction of the free chlorine residual by sunlight. In the stabilization process, a portion of the chlorine residual is temporarily bonded to the cyanuric acid molecule. Consequently, it's protected from the destructive effects of sunlight. The nature of this bond is such that the chlorine demand is imposed upon the

system and continues to be released as long as a demand exists. The role of chlorine in pool water sanitizing and the process of stabilization can be better understood when considered as part of a generalized pool chemical reaction. In swimming pool waters, the free chlorine - HOCl - may be consumed in several ways:

1. By destroying bacteria and algae introduced by swimmers and by wind and rain-borne contamination.
2. By reacting with reduced metals such as  $\text{Fe}^{++}$  to produce the oxidized  $\text{Fe}^{+++}$  and chlorine ions.
3. By the action of the ultraviolet energy of sunlight, which converts free available chlorine to the inactive chloride ion.
4. By oxidizing nitrogenous compounds such as ammonia ( $\text{NH}_3$ ) and urea introduced into the water as components of perspiration, urine and other bodily excretions.

### **Maintenance of Free Available Chlorine Residual**

Recommended level: 1 ppm to 3 ppm of free available chlorine

Ok, we've heard about sanitizers. They sound good. But how are you convinced? Simple. By this side-by-side test....

Pre-conditioning the pool with 30ppm of conditioner, and using a sanitizer to maintain that minimum, automatically provides protection for a pool against the effects of sunlight. The benefits of this system of pool treatment are best illustrated in comparative tests of chemical consumption. In this test, the effects of sunlight on pools treated once a day is dramatically demonstrated.

- Identical 5000-gallon pools, located side by side to eliminate variations in climatic exposure, were monitored over a period of several days.
- In an unstabilized pool, an inorganic hypochlorite was added at the label directed dose of 4 ppm FAC (84gm/3 oz.). The other pool was stabilized and treated with stabilized granular ( $\text{NaDDC} \cdot 2\text{H}_2\text{O}$ ) at 1ppm residual, so  $\frac{1}{2}$  of the original dose of the product was added.
- 24 hours later there was no residual in the hypochlorite pool. So, a double dose of product was added. The stabilized pool still contained the desired 1ppm residual, so  $\frac{1}{2}$  of the original dose of the product was added.
- This procedure was repeated for 4 days. At the end of the test, the hypochlorite pool, even with 16ppm (336 gm/12 oz.) of product could not hold a residual over one day. The stabilized pool, with less than  $\frac{1}{3}$  ppm (7 gm/0.2 oz), still maintained its residual.

These figures were obtained with no bathers using the pools. The chlorine from the unstabilized pool was consumed strictly by the action of sunlight.

### **Dosage Rate For Conditioner**

Recommended maintenance level: 30-ppm minimum

During a pool season, the conditioner level in the water may decrease from leakage, bather activity causing splash out or drag out, and normal maintenance operations such as vacuuming and filter back washing.

To maximize the advantages of stabilization, the following quantities of conditioner should be added to maintain a 30-ppm minimum level. Because of the slightly acidic pH of conditioner, addition of a small quantity of pH plus may be necessary to maintain pH at the desired level.

4.2 ounces per thousand to obtain 30 ppm

1 ounce per thousand = 7 ppm

Should the conditioner concentration increase to a regulatory agency mandated maximum level, it can be lowered by dilution with fresh make-up water.

## ONE IN A MILLION

Operating a pool is economical primarily because of the efficiency and versatility of free available chlorine. This disinfectant performs all the functions necessary to maintain sanitary, high quality pool water. It does this in part per million (ppm) concentrations - which is an extremely small quantity in relation to the results provided. When we say small, we mean it. A ppm is actually equivalent to: parts per million a unit of concentration equivalent to:

1 inch in 16 miles 1 minute in 2 years 1 needle in 2000-pound haystack and 1 penny in 10,000 dollars.

To understand the economy this provides, consider the amounts of chlorine that'd be required to operate a pool if free available chlorine were only available at percent concentrations. A percent is 10,000 greater than a ppm. The truth is, there'd be very few pools if 1% or even 0.1% FAC, rather than 1 ppm, was necessary for successful pool operation. Speaking of success, it's time to meet a good friend of yours.

## Algae - One of the Best Salesmen

Algae are the most common fouler of pools. When pool owners panic and run screaming to a pool pro for help, algae are most frequently the cause. That's why we call it one of the best salesmen. You must deal with an algaecide. Actually, in addition to getting rid of algae, one of the most effective uses of algaecide is to extend the effectiveness of chlorine residual. While chlorine is an algaecide, it's wise to add additional quantities as a backup, a maintenance dose.

## **What is algae?**

Algae are small plants that propagate by air-borne spores. They enter swimming pools and quickly turn the water green. When conditions favor their growth, they can cause black and/or green spots on pool walls. Heavy rain, intense sunlight, and presence of nitrogenous material all contribute to algae bloom - as the rapid growth of algae is called. Sometimes algae bloom results in a sharp rise in pH, as the algae consume carbon dioxide in the pool water. If algae bloom is present, super chlorination should be used. Then an algaecide will control it, and prevent its reoccurrence. The best insurance against algae? Maintain a free chlorine residual in the pool at all times. An effective way to do this is to sanitize with stabilized pool chlorinating concentrates, and add algaecide according to the directions on the label.

## **Water - It Only Looks Simple**

In addition to chlorine sanitizing, there are other water factors to consider. The most common are:

1. pH- a system for measuring the acidity or alkalinity of water. Readings above 7 are alkaline: readings below 7 are acidic.
2. Total alkalinity- a measure of the buffering capacity of pool water.
3. The amount of calcium or magnesium dissolved in pool water. High levels contribute to scale deposits.

Let's take a closer look at these elements.

pH. Many things can change the pH of pool water from the desired range of 7.2 - 7.8. Rain, dust and bather wastes can all raise or lower pH and necessitate frequent testing. Even more significant is the pH of the sanitizer used. Obviously, a sanitizer that has a pH near the desired range will be far more effective and convenient to use. stabilized granular, with a pH of 6 - 7, will certainly have very little effect on the pH of the pool. Consequently, the residual it provides will be more effective with fewer adjustments. Stabilized tablets, although low in pH, also have a minimal effect. That's because their high available chlorine and stabilization means far less is needed to provide effective sanitation. Chlorine gas, calcium hypochlorite, and liquid bleach all require much larger amounts of pH adjustment, because their pH is far from the desired operating range. Pool owners who insist on using these sanitizers should be advised of the need for pH adjusting chemicals and testing, as their pH is far from the desired operating range. They should also be advised that pH plus and pH minus are excellent products for raising or lowering pool water pH to the proper range. Recommended pH range is 7.2 - 7.8 and must be maintained within the indicated range because of its impact on chlorine efficiency, bather comfort, corrosion and scaling. Since total alkalinity affects the amount of pH adjusting chemical to be added, it should first be adjusted to the 80-125 ppm range.

**TOTAL ALKALINITY.** Control of pH can be simplified by maintaining total alkalinity in the range of 80- 125. Total alkalinity is composed of carbonates, bicarbonates, and hydroxides, and functions as a buffer to help keep pH in the proper range.

\* If total alkalinity is too high, you have staining, scale and difficulty in adjusting pH.

\* When total alkalinity is too low, there's corrosion and pH bounce.

Total alkalinity is easily measured with a test kit, and can be adjusted with alkalinity control or acid according to label directions. Total alkalinity, in addition to buffering, provides some control over the corrosive or scaling tendencies of the water. The recommended total alkalinity level should be 80-150ppm. Total alkalinity is a measure of the buffering capacity of pool water. If total alkalinity is too low, pH bounce and erratic behavior are encountered. Total alkalinity can be raised by the addition of alkalinity control. If total alkalinity is too high, it becomes difficult to adjust pH. Also, staining and scaling may occur. To reduce a high total alkalinity to 80ppm, you add granular pH minus or muriatic acid (not more than 1 pint at a time).

**WATER HARDNESS.** Another factor in pool water problems is hardness, a measure of the calcium and magnesium content of the water. All water contains some natural hardness. The amount will vary regionally, and from source to source within a region. A certain amount is necessary in water to control its tendency to dissolve. If too little is present in a pool, the water will attack the materials of construction to satisfy its appetite. Hardness treatment will increase low water hardness and prevent etching, pitting and corrosion of surfaces and metallic components in such a situation. Scaling occurs if too much hardness is present. This is visible as crusty gray deposits and cloudy water, or visible as deposits in piping. A pool's pipes, designed to accommodate a certain water flow at a certain pressure, will obviously not function properly if their diameters are decreased by scale formation on their inner surface (white rings inside the pipe). It's a bit like a pool's hardening of the arteries. Scale on pool surfaces is unsightly and unattractive. Scale in pool plumbing is disastrous and expensive, since it interferes with the circulation and filtration of the pool water.

## YOU ARE WHAT YOU EAT: A LOOK AT CHLORINE CONSUMPTION

As you know, chlorine is very rapidly consumed by the action of sunlight in a swimming pool. Any chlorinated sanitizer will produce HOCl, but up to 97% of that residual can be lost in 2 hours! What does this mean in actual pool operation? Well, when 4-5ppm of free available chlorine is added as calcium hypochlorite at 6 am, it'll be completely gone by 12 noon. Whether or not anyone uses the pool. This same wasteful chlorine consumption occurs with chlorine gas and sodium hypochlorite. For the bulk of their swimming time, Mr. Or Mrs. Pool owner really have no assurance that the pool is sanitary, or that contamination will be rapidly eliminated as it enters the pool. What to do? The conscientious pool owner, aware of the importance of the free available chlorine residual, could operate his pool satisfactorily if he tested the water at noon, and added another 4-5 ppm residual for safe afternoon swimming. He'd then have to repeat

the process at 6 pm so the entire family could enjoy the pool in the evening. Three times a day. Whew! Or, he could install a bulky and complex chemical feeding system to constantly add sanitizer. He would also probably need a separate feeder to add a pH-adjusting chemical, while large quantities of the unstabilized sanitizer are being added. Sound unwieldy? It is. And there's a better way. You guessed it. Our pool owner could use a sanitizer, add the label-directed 1-1.5 ppm of free available chlorine, and be assured that it would keep the pool water clear and sparkling.

## **Fresh Water And TDS**

TDS is not an abbreviation for "Tough day on Saturday", or "Take a dip Steve". It stands for Total Dissolved Solids. TDS are a measure of all the dissolved chemicals in the water. Whether they're natural components of source water, residues of treatment chemicals, bathers' wastes, or wind and rain-borne atmospheric pollutants, they stay in the water and concentrate. Eventually, TDS will cause staining, scaling, reduced chlorine efficiency, and erratic pool behavior. All pool water contains total dissolved solids. If a drop of TDS water could be magnified, it might show Ca (calcium) and Na (sodium), representing dissolved chemicals. Although a dissolved chemical is not visible to the naked eye, it does occupy space in the water. Take table salt, for instance. It's visible in the shaker and invisible in a water solution - but it reappears if the water is boiled away. It hasn't disappeared, it's just been dispersed as submicroscopic particles called ions. In ideally stabilized water, HOCl has a direct route to reach algae, bacteria and germs that it must destroy to provide sanitary water. The ions of the dissolved solids are widely dispersed, and don't hinder this action. Unfortunately, water doesn't remain in this ideal condition for very long. Even the residues of sanitizers consumed in the various categories of the California field test produced substantial amounts of dissolved solids during one season of treatment. And these TDS accumulations are the chemical residues from sanitizer treatment only. Other materials add even more dissolved materials.

## **ALPHABET SOUP**

It's interesting to note that stabilizing and using chloroisocyanurate produces the least amount of TDS. When more chemicals are required, more residues result. Eventually, you get microscopic alphabet soup. Several seasons of adding chemicals and bathers to water that are already exposed to a variety of natural contaminants can create a very crowded body of water. Obviously, as this alphabet soup gets more crowded it's difficult for HOCl to perform efficiently. And algae, bacteria and germs that are not eliminated will cause problems. It's difficult to predict exactly how fast TDS will accumulate, and at what concentration they'll cause trouble. But it's been estimated by the NSPI chemical treatment and process committee that TDS should be maintained at less than 1500 ppm. Concentrations in excess of that may cause problems.

NOTE: When problems with TDS occur, untrained homeowners and overworked service people often find a convenient culprit in overstabilization. (There's really no such thing.) Cyanuric acid is easy to measure, and gives a test result that can be interpreted

individually, to explain almost every water quality problem. A cloudy, green pool will almost certainly have one or two ppm in excess of some arbitrary maximum. The problem pool water will be dumped to lower the cyanuric acid content, and the problem will magically disappear.

## WHAT IS THE PROBLEM, ANYWAY?

What isn't usually recognized is that any dissolved solids, chloramines, or pH buffers will be correspondingly reduced when a pool is dumped. It's impossible to remove only one kind of dissolved material in water that's all gone. Total dissolved solids have not received the attention they deserve for causing pool problems, because they aren't easy to measure - and there's a tendency to forget they're in the water. Additionally, they've never received the kind of study and publicity that have surrounded cyanuric products. It has been proven that cyanuric acid causes no ill effects in pool water... but that it may, by it's accumulation, signal the onset of problems due to TDS in the pool. Apparently this proof has been convincing, since the leading proponent of the overstabilization theory has built a cyanurate plant!

## LESS IS MORE.

The fact is, there's only one practical way to remove dissolved solids from a pool. That's to remove a portion of the water in which they're dissolved. Removal of 100 gallons of water removes 1.7 pounds of dissolved solids from a 10,000 gallon pool containing 2,000 ppm TDS. If the cost for control of TDS accumulation is calculated, the partial water removal procedure becomes the ultimate bargain in pool operation.

- The recommended rate of water removal per week is 1-3%.
- In a 10,000-gallon pool, this represents 100 gallons per week, or 4,000 gallons in a ten-month season.
- At .53 per 1000 gallons, this would cost \$2.12. Since many municipalities levy a sewage charge of 120% of the cost of the water, an additional \$2.54 is added.
- The total cost for replacing 40% of the used water in the pool is \$4.66.

If this cost seems excessive, compare it to the initial investment in the pool, the cost of chemicals that don't perform efficiently, and the expense of dumping, acid washing, refilling and balancing. You'll find that water is the cheapest chemical that can be added to a pool.

## Chloramines - The Great Imposter

Since all chlorinated sanitizers react with water to produce HOCl, chlorine consumption depends on the amount of contamination that is present - not the brand that's used. Enough sanitizer must be added to meet the chlorine demand of the water before a measurable residual can be maintained. This amount depends on the amount of contamination present in make up water, plus whatever is added by bather loading, rain, dust and other external sources. One particularly troublesome type of contamination is



nitrogenous waste from bathers bodies. Whether they are as simple as ammonia in urine, or as complex as the components in perspiration or saliva, they present special problems when they accumulate in pool water. These contaminants react with HOCl to form compounds called chloramines, or combined chlorine.

## **CHLORAMINES**

The combined chlorine reaction begins with one unit of ammonia, combining with one unit of HOCl to form monochloramine ( $\text{NH}_2\text{Cl}$ ). This reacts with another unit of HOCl to form dichloramine and finally with a third unit of HOCl to produce trichloramine ( $\text{NCl}_3$ ). We're not through yet. It takes a fourth unit of HOCl to finally convert the original molecule of ammonia into harmless nitrogen gas ( $\text{N}_2$ ), water and chloride ion ( $\text{Cl}^-$ ) and a fifth unit of HOCl before a free available chlorine residual can be measured. These chloramines cause plenty of trouble in pool water. Why? Because they are stable and persistent. The monodi and trichloramine from this first unit of ammonia will survive and accumulate with the chloramines formed from subsequent units of ammonia. This is actually chlorine consumption, because HOCl combined with ammonia forms chloramines. Chloramines have very poor sanitizing power, so algae and bacteria can grow. In fact, they have such poor pool sanitizing power that they would be rated at only 0-10 on a relative activity scale with HOCl rated at 10,000. Quite a difference. It's been estimated that chloramines could provide germ free water if they were present at a concentration of at least 25 - 50 ppm. But this would create additional problems in a swimming pool, because they're very pungent and irritating, causing eye irritation and chlorine odors at very low concentrations.

## **OTO**

### **OTO Method of Determining Chlorine Levels**

For many years, the most common test for residual chlorine has been the OTO method. It is based on the fact that a clear, organic solution called orthotolidine (OTO) turns yellow in the presence of free or combined chlorine. Increasingly greater concentrations heighten color intensity until a deep orange or red color is reached at extremely high chlorine levels. OTO test results do not successfully differentiate between FAC and combined chlorine.

OTO testing, while still available in the U.S., is regarded by authorities as out-of-date or inferior to DPD testing. In many public health jurisdictions, the DPD test has been made mandatory.

This OTO method has some advantages that have made it popular and widely used. It also has some major deficiencies. The fact that it cannot easily distinguish free from combined chlorine makes it a very doubtful aid to pool operation. Even worse, it creates a false sense of security, leading to erroneous diagnosis of pool problems, which delays remedial action. The pool owner could test once, twice, or three times daily and still have no idea whether enough free available chlorine was present to protect the quality

of the water. A 1-ppm residual measured by OTO will provide far less protection to pool than a 1-ppm residual measured by the DPD method.

## **DPD**

### **DPD Methods of Determining Chlorine Levels**

The DPD method uses standardized liquid or tablet reagents containing diethyl-p phenylenediamine indicators. The advantage of DPD testing is that it can be used to differentiate between free and combined chlorine. DPD tablet reagents are highly stable and easy to work with. They come in foil packets for easy handling and have an extended shelf life. DPD reagents produce a pink-to-red color change that is easy to read.

Separate DPD tablets or liquids are used to test for residual chlorine in its various forms: Free available chlorine (FAC), using DPD tablet #1 or liquid reagents #1 and #2; total chlorine, using tablets #1 and #3 or liquids #1, #2 and #3; and combined chlorine or chloramine, by subtracting the free reading from the total. Other tablet numbers are normally not used in pools. No. 2 is used for monochloramine, and #4 is for total chlorine only.

### **Free Available Chlorine (FAC) Test - Using DPD Tablets**

1. Wash the test vial with pool water. Wash stirring rod if used.
2. Fill the vial with pool water to the graduated line on the side of the tube.
3. Add one DPD tablet #1.
4. Cap the top of the vial (not with fingers). Shake well or use stirring rod to dissolve the tablet. Make sure it is dissolved, although some residual on the bottom is normal.
5. Quickly compare the resulting color with the test-kit standards to determine the free available chlorine value.

Test kits with precise liquid standards, closely graduated, are available. Some kits use clear water vials next to the test vial to make the optical light paths similar when judging color standards.

### **Total Chlorine Test Using DPD Tablets**

1. Follow steps 1 through 5 from the above for the free available chlorine DPD test.
2. Add one DPD tablet #3 to the FAC test sample.
3. Cap the top of the sample cell and shake or use the rod until the tablet dissolves.
4. Compare the resulting color with the test-kit standards to determine the level of total chlorine.

## Combined Chlorine Calculation

Calculate the combined chlorine (chloramine) level by subtracting the free available chlorine level from the total chlorine level.

## Dilution Method

Often a test sample of free available chlorine (FAC) reads at the upper limit of the test kit's color comparator. This sample should be regarded as possibly containing a chlorine level that is above the test kit's ability to measure. In this case, the dilution method of testing should be followed.

Using the dilution method, a vial is filled with  $\frac{1}{2}$  sample water and  $\frac{1}{2}$  distilled water (or bottled water that does not contain any ammonia or chlorine). The test is performed as above, but the results should be doubled. Other dilutions can be used, such as  $\frac{1}{3}$  sample water and  $\frac{2}{3}$  distilled water - in this case, the results should be tripled.